SURVIVAL OF LIGNIN-DERIVED STRUCTURAL UNITS IN ANCIENT COALIFIED WOOD SAMPLES

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ABSTRACT

Analysis of five Cretaceous-age and one Carboniferous-age fossil wood samples of lignite rank by pyrolysis-gas chromatography-mass spectrometry has revealed the presence of lignin-derived compounds such as phenols and methoxyphenols. In Cretaceous lignitic wood, the various methoxyphenols were of the same suite as those produced from pyrolysis of modern lignin and degraded wood. Indications are that the lignin structural units of Cretaceous lignitic wood samples are preserved to varying degrees. In Carboniferous lignitic wood only traces of methoxyphenols were detected, but phenols were abundant. This is the first indication that lignin-derived methoxyphenols can survive in geological materials as old as the Carboniferous.

INTRODUCTION

Lignin is a major biochemical component of woody tissue; however, it rarely survives early stages of coalification. Biochemical and chemical alteration during burial limit the extent to which lignin biomarkers can be preserved and recognized in the geologic record. Lignin-derived compounds have been observed in pyrolysis products of low rank coals and associated woody tissue[1-5]. Mycke and Michaelis[6] isolated lignin-derived methoxyphenols from a Miocene coal by catalytic hydrogenolysis. Sigleo[7,8] reported the presence of phenolic compounds derived from alteration of lignin in pyrolysis products of silicified woody tissue as old as Triassic age. However, no trace of methoxyphenols, that would clearly relate back to lignin structures, could be identified in Sigleo's samples. Hayatsu et al.[9] similarly reported the presence of lignin-derived products from copper-oxide oxidation of several coal samples. They, too, were unable to identify methoxylated phenols in their products. Recently, Nip et al.[2] subjected two lignite samples, one of Paleocene age and the other of Eocene age, to Curie-point pyrolysis-mass spectrometry. The data indicated only traces of methoxyphenols. They were puzzled by the low abundance of phenols in general, because the petrographic data indicated large amounts of huminite derived from woody tissue.

The most definitive identification of lignin-derived pyrolysis products in coalified wood samples as old as Paleocene age was reported in a study of coalified wood by Stout et al.[4]. They identified numerous lignin-derived methoxyphenols in angiospermous and gymnospermous wood samples from various lignites by Curie-point pyrolysis-gas chromatography-mass spectrometry. In a study of lignitic gymnospermous wood samples of Cretaceous and younger ages by analytical pyrolysis[5], we reported the presence of methoxyphenols in the pyrolyzates. Many of these methoxyphenols had associated propenyl side chains indicative of the presence of well-preserved lignin residues.

In an attempt to delineate the degree of preservation of lignin in coal, we examined numerous coalified wood samples ranging from Carboniferous to Holocene age. The samples were initially screened by solid-state C-13 nuclear magnetic resonance to detect the possible presence of methoxyl carbon. Once such carbons were detected, the samples were subjected to analytical pyrolysis to determine the content of methoxyphenols which would provide an indication of the state of preservation of the lignin-derived structural units. We report here on the
identification of lignin-derived methoxyphenols in the coalified wood samples selected for analytical pyrolysis.

SAMPLES AND METHODS

Samples of coalified wood (xylem) were obtained from Carboniferous and younger strata in various locales. A sample of coalified wood was collected by D. Gottfried (U. S. Geological Survey) from the Magothy Formation (Upper Cretaceous) at the C&O canal near Bethel, Maryland. Byrd Stadium lignitic wood was collected by the late I. A. Breger (U. S. Geological Survey) from an excavation for Byrd Stadium on the campus of the University of Maryland. The coalified logs at this site were buried in an upright position in sediments of the Potomac Group (Lower Cretaceous). Wayne Newell (U. S. Geological Survey) graciously provided a sample (Stafford lignite) of coalified wood buried in sediments of the Potomac Group (Lower Cretaceous) near Stafford, Virginia. Another sample was obtained by Roger Thomas (U. S. Geological Survey) from the Patapsco Formation of the Potomac Group (Lower Cretaceous) near the intersection of I-95 and I-695 in Landsdowne, Maryland. Another sample (Long Island lignite) was obtained by Byron Stone (U. S. Geological Survey) from probable Pleistocene clay in the Nassau Brick Co. clay pit on Long Island, New York; the sample probably was reworked from the Magothy Formation (Upper Cretaceous). Finally, a sample of coalified wood was obtained from the collection of the late I. A. Breger, and this sample was from the Carboniferous lignite deposits of the Moscow Basin, USSR, Kurovskaya mine No. 1. All samples were essentially of lignite rank as partially demonstrated by the elemental data in Table 1.

Table 1. Elemental compositions (dry mineral-matter free) for coalified wood samples.

<table>
<thead>
<tr>
<th>Lignite Sample</th>
<th>Wood type</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stafford</td>
<td>G</td>
<td>74.9</td>
<td>4.98</td>
<td>0.58</td>
<td>18.9</td>
</tr>
<tr>
<td>Long Island</td>
<td>NA</td>
<td>61.1</td>
<td>4.57</td>
<td>0.33</td>
<td>34.0</td>
</tr>
<tr>
<td>Patapsco</td>
<td>G</td>
<td>65.7</td>
<td>5.00</td>
<td>0.27</td>
<td>29.3</td>
</tr>
<tr>
<td>Byrd Stadium</td>
<td>G</td>
<td>59.2</td>
<td>3.17</td>
<td>0.21</td>
<td>36.3</td>
</tr>
<tr>
<td>Magothy</td>
<td>G</td>
<td>72.2</td>
<td>4.43</td>
<td>0.21</td>
<td>22.0</td>
</tr>
<tr>
<td>Moscow Basin</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

G: gymnospermous wood
NA-data not available

Pyrolysis-gas chromatography-mass spectrometry was performed on a DuPont 490B gas chromatograph-mass spectrometer system interfaced with a Technivent Vector 1 data system and a Chemical Data Systems model 120 pyroprobe. Pyrolysis-gas chromatography was performed with a Perkin-Elmer Sigma 2B gas chromatograph interfaced to the pyroprobe. The fused silica column was a 50% phenylmethylsilicone phase available from Hewlett-Packard. Operating conditions and specific methodologies have been given in a previous report[5].

The presence of lignin structural units was confirmed by pyrolysis-gas chromatography-mass spectrometry using comparisons of mass spectra to library spectra, to spectra of authentic standards, and to published mass spectra of lignin phenols[10].
RESULTS AND DISCUSSION

Pyrolysis of Cretaceous lignitic xylem has been shown in a previous report[5] to yield abundant quantities of methoxyphenols derived from the lignin residues preserved in the lignitic woods. The state of preservation can be determined by the abundance of methoxyphenols relative to other altered lignin byproducts such as the phenols and catechols. Figure 1 shows the pyrograms for two samples representative of most of the Cretaceous age lignitic wood in which the state of preservation of lignin varies widely. Peaks for guaiacol, 4-methylguaiacol, 4-vinylguaiacol, 4-ethylguaiacol, eugenol, cis-and trans-isoeugenol, vanillin, and acetoguaiacene are clearly the major products in the Long Island lignite, the one representative of lignitic wood samples in which lignin-derived structures are believed to be the least altered. These specific methoxyphenols are clearly derived from lignin precursors or partially altered lignin that has survived in the lignitic wood samples. Extensively altered lignin products such as phenol, the cresol isomers, catechol isomers, and the alkylphenols are also major components of the pyrogram, but they are subordinate to the methoxyphenols in the Long Island lignite. In the Magothy lignite, the phenols and cresols are dominant over the methoxyphenols, indicating that the lignin residues in this sample are significantly more altered than in the Long Island lignite. The degree of lignin preservation varies widely among the lignitic wood samples. In wood samples of subbituminous rank, methoxyphenols have not been detected; the dominant pyrolysis products are phenols and cresols[5].

Analytical pyrolysis of gymnospermous lignin that is minimally altered has been shown to yield the same products as those mentioned above for the least coalified wood samples, although the relative peak intensities may be different[10,12,13]. Figure 2 shows a pyrogram for a gymnospermous log (Atlantic White Cedar, Chamaecyparis thyoides) buried in peat from the Great Dismal Swamp, Virginia. Previous studies have shown that most of the cellulosic components of this sample have been degraded microbiologically, leaving lignin relatively unaltered[14]. The pyrogram confirms this by showing a product distribution that is typical of lignin[12], although the broad peak for levoglucosan indicates a small amount of cellulosic material is present. The four largest peaks are for 4-methylguaiacol, 4-vinylguaiacol, guaiacol, and trans-isoeugenol in decreasing order of intensity. The relatively high abundance of methoxyphenols having the 3-carbon side chain (eugenol, the isoeugenols, coniferaldehyde, and guaiaclpyropan-2-one) and the low abundance of methylvanillate, vanilloyl methyl ketone, and vanillic acid is evidence that the lignin is not altered extensively[12]. Also, the presence of only trace levels of phenols, cresols, and catechols in the buried log is evidence for unaltered lignin.

The lesser quantities of methoxyphenols having the 3-carbon side chain, relative to the other methoxyphenols, in the Cretaceous lignitic wood samples, compared to the modern buried cedar, are an indication that the lignin in the Cretaceous samples has been altered significantly. For example, the ratio of peak intensities, for guaiacol/trans-isoeugenol, is 1.3 for the modern buried cedar, whereas the Cretaceous lignitic samples have values that range from 4.8 to 11. This more than five-fold increase in the ratio is indicative of the fact that the lignin molecules in the lignitic woods are altered at the side-chain sites.

Although the lignin-derived methoxyphenols are important components of the pyrolysis of Cretaceous lignitic wood samples, phenols, catechols, and methylated phenols are equally important. The ratio of phenols-catechols to methoxyphenols ranges from 1.0 to 4.9 in the lignitic woods. In the buried cedar, this ratio is 0.10, indicative of the fact that lignin-derived methoxyphenols are the principal constituents and the phenols and catechols, the products of altered lignin, are subordinate. Sigleo[7] suggested that phenols, cresols, and catechols in pyrolysis products of 200-million-year-old petrified wood are derived from altered lignin. We support this conclusion, primarily because lignin is the most likely source of phenols in the lignitic
woods and because of the abundance of lignin-derived methoxyphenols which are co-produced during pyrolysis.

The pyrolysis data for the lignitic wood from the Moscow Basin are shown in Figure 3. The major pyrolysis products are alkylbenzenes, but phenol and alkylphenols comprise major peaks in the pyrogram (Figure 3a). Only a trace of methoxyphenol (Figure 3b) and methylmethoxyphenol (Figure 3c) could be detected in the sample. However, the trace presence of these two methoxyphenols is clear indication that lignin-like material was present in the wood and that only a trace of it remains, albeit in a highly altered form. Thus, the presence of the methoxyphenols in pyrolysis products indicates that lignin-derived components have survived for approximately 300 million years. It is interesting that three isomers of methoxyphenol can be detected in the selected ion trace of m/z 124 (Figure 3b). That these specific peaks were indeed methoxyphenols was determined by retention times and by examination of the fragment ions at m/z 109 and 81. Similarly, the verification of the presence of methylmethoxyphenol was made by retention time and by examination of fragment ions at m/z 123 and 95. Only one isomer of methylmethoxyphenol was detected (Figure 3c) and its retention time on the column corresponds to that of 4-methylguaiacol. Direct comparison of mass spectra to library spectra of authentic methoxyphenols was not possible due to the trace quantities and the complexity of the pyrolysis mixture in the retention-time windows for elution of the methoxyphenols.

Phenol, the cresol isomers, and the dimethylphenols, major pyrolysis products in the Moscow wood sample, are probably also derived from lignin precursors that have been altered through coalification reactions. Hatcher et al. [5] have shown that an increase is observed in the relative proportion of phenols and cresols as rank of coalified wood samples increases to subbituminous coal. Comparing the pyrolysis products from the Moscow wood to other coalified wood samples of Hatcher et al. [5] allows us to deduce that the Moscow wood is more similar to coalified wood of subbituminous rank than it is of coalified wood of lignite rank, assuming that its lignin was originally similar to lignin in Cretaceous or younger woods.

CONCLUSIONS

The analysis of lignitic woods by analytical pyrolysis has shown that lignin structural units can be preserved as biomarkers in samples as old as Carboniferous age, or approximately 300 million years. At least half or more of the pyrolysis products in lignitic wood of Cretaceous age are methoxyphenols characteristic of lignin. The product distributions in these Cretaceous samples indicate that the lignin is mainly altered in the side chains. Phenols, cresols, catechols, and other methylated phenols account for the remainder of the pyrolysis products. It is likely that these products are also derived from lignin, especially lignin that has been altered by coalification reactions.

ACKNOWLEDGMENTS

We thank our colleagues at the U. S. Geological Survey, Roger Thomas, David Gottfried, Byron Stone, and Wayne Newell, for providing samples for this study.

REFERENCES

Figure 1. Pyrolysis-gas chromatography of two Cretaceous lignitic wood samples. Numbers above the peaks refer to identified pyrolysis products listed to the right.

1. Phenol
2. o-Cresol
3. m & p-Cresol
4. Guaiacol
5. C6-Benzene & C4-Phenol
6. 3,5-Dimethylphenol
7. 2,3-Dimethylphenol
8. 4-Methylguaiacol
9. Catechol
10. 4-Ethylguaiacol
11. Methylcatechol
12. 4-Vinylguaiacol
13. Eugenol
14. cis-Isoeugenol
15. trans-Isoeugenol
16. Vanillin
17. Acetguaiacone
18. Vanillic Acid
19. Coniferaldehyde

Figure 2. Pyrolysis-gas chromatography of Atlantic White Cedar from the Dismal Swamp, VA. Numbers above the peaks refer to identified pyrolysis products listed to the right.
Figure 3. Pyrolysis-gas chromatography-mass spectrometry of the coalified wood from the Moscow Basin lignite. Trace A represents the total ion chromatogram (TIC), B represents the mass chromatogram for m/z 124, and C represents the mass chromatogram for m/z 138. Peak assignments are listed.
The high water content of Victorian brown coals at approximately 60% is characteristic of these coals but its removal has proved economically disadvantageous. It has recently proved possible, however, to reduce the water content to approximately 10% in a process of densification (4) which is under patent protection (5). The densified brown coal (DBC) produced compares favourably in its Net Wet Specific Energy with a black coal and retains all the other gross characteristics of the raw brown coal.

Densification can also be regarded as a dewatering process. The scheme of production of a DBC is shown in Figure 2 (4) whilst Figure 3 illustrates the loss of moisture with time at ambient temperature and relative humidity. This release of water from the pores of the coal whilst initiated by the attritioning procedure is accompanied by chemical cross-linking reactions and the main thrust of this paper is to explore the chemical aspects of densification.
<table>
<thead>
<tr>
<th></th>
<th>Brown coal Morwell, Vic.</th>
<th>Black coal Tarong, Qld.</th>
<th>Densified brown coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>59% wb</td>
<td>5.2% adb</td>
<td>15.9% adb</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>49.2% db</td>
<td>29.7% db</td>
<td>48.9% db</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>48.8% db</td>
<td>40.9% db</td>
<td>49.1% db</td>
</tr>
<tr>
<td>Ash</td>
<td>2.4% db</td>
<td>29.4% db</td>
<td>2.4% db</td>
</tr>
<tr>
<td>Total sulphur</td>
<td>0.3% db</td>
<td>0.42% db</td>
<td>0.3% db</td>
</tr>
<tr>
<td>GSE</td>
<td>27.2 MJ/kg daf</td>
<td>31.98 MJ/kg daf</td>
<td>27.2 MJ/kg daf</td>
</tr>
<tr>
<td>NWSE</td>
<td>8.4 MJ/kg</td>
<td>21.3 MJ/kg adb</td>
<td>22.0 MJ/kg adb</td>
</tr>
<tr>
<td>Bulk density</td>
<td>1130 kg/m³</td>
<td>1200-1700 kg/m³</td>
<td></td>
</tr>
</tbody>
</table>

wb - wet basis. adb - air dry basis. db - dry basis. daf - dry ash free. GSE - gross specific energy on a dry ash free basis. NWSE - net wet specific energy.

Victorian brown coals are not only chemically complex in components but are physically porous. Kneading will reduce the particle size of the coal and liberate water from the pore structure forming a slurry or paste. Figure 4 illustrates the effects of kneading on the changes in diameter of 10mm pellets on drying. The shrinkage observed is a consequence of loss of water content but also of the development of considerable strength in the pellets as Figure 5 illustrates. Morwell DBC pellets can sustain a load of 280kg at a crush strength of 35MPa. There is a marked difference between the crush strengths developed in DBC from Loy Yang and Morwell coals (Fig. 5) although particle size is the same for both coals. This difference is reflected also in porosities after densification (37% volume porosity for Loy Yang coal versus 14.6% for Morwell) which appear to be the inverse of crush strengths (5.7 for Loy Yang versus 18.5 MPa for Morwell). Pellet shrinkage and the development of crush strength with time can be interpreted as chemical cross-linking reactions drawing microdomains together and in the process excluding water and densifying. Strong pellets may develop cracks on the surface and the crush strengths measured reflect the point of greatest weakness. The shattered fragments retain their strength however.

In seeking to explain these physical changes in terms of chemical reactions it is unlikely that only one class of reactions is involved; rather a range of chemical interactions must be considered. It is known that Victorian brown coals do contain stable free radicals and that as the coal particles are brought closer together by the physical kneading, radical couplings could occur which include cross-linking reactions. We have often noted that a small crush strength maximum develops in the early stages of attritioning which probably occurs as a result of this type of bond formation. Additional forms of bonding would involve ionic reactions, the most likely centres of reaction being carboxyl groups, phenols and activated aromatic systems. The strong pH control of development of crush strength suggests that ionic reactions are the probable cross-linking reactions. Figures 3 - 5 show how densification is coal dependent, but Figure 1 illustrates how compositional differences will also be lithotype-dependent so
that the averaged reactivities of ROM coals integrate several variables.

A dominating parameter in the control of crush strength ($G_C$) of DBC pellets is the pH of the raw coal (Figure 6). Coals have a natural pH which may vary depending upon storage time and exposure to air. The more acidic the coal, the smaller the crush strength of the DBC. However, basic additives can raise the crush strengths as illustrated for NaHCO$_3$ as an additive to Loy Yang coal (Figure 6). Loy Yang is a naturally acidic coal (pH 3.2) but shows a dramatic change in $G_C$ with increase of pH. NaOH, a strong base, when used as an additive gives a DBC showing a maximum $G_C$ at approximately pH 6. This is close to the pH (5.3) determined for ROM Morwell coal and thus explains why a strong base additive does not usefully improve its performance during densification.

Clearly, (i) the O-/OH and COO-/COOH ratios in the brown coals, (ii) the absolute abundances of these functional groups, and (iii) their sensitivity to pH are major controlling factors in determining crush strength. In turn these oxygen functional groups can be expected to interact by substituting in activated aromatic systems in the coal. Again, pH will be important in facilitating such interactions. The molecular complexity of the likely reactions will mean that at best a range only of reactions and reactivities will be observed. Given that oxygen functionalities can be expected to play a significant role in densification, one probe would be to sequester acidic hydroxyl groups and observe the effect on crush strengths on densification.

Methylation of brown coals using tetrabutylammonium hydroxide/methyliodide as the methylating agent has an advantage that it swells the coal and utilizes the water already inherent in the coal. Methylation affects densification in two ways: first, the DBC formed is weak (Table 2). By removing many of the acidic OH groups through methylation they are unable to form new chemical bonds, although some activation of the attached ring systems by methoxy substituents will be retained. The low $G_C$ values recorded can be interpreted as a consequence of the inhibition of the intermolecular bonding between particle surfaces. The second observation was that the paste produced on kneading was very moist indeed and consequently generates very little plastic strength. Methylated coal had lost most of its capacity to hold water in its pores presumably because of the reduction in H-bonds to oxygen groups in pore wall surfaces.

The decrease in crush strength maximum of the DBC (Figure 5) on extended drying we believe to be real and probably results from decreased H-bonding. This observation as well as those cited above are consistent with our hypothesis that cross-linking chemical reactions involving acidic hydroxyls and activated aromatised ring systems are involved in the development of microdomains between coal particles. They are also primarily involved in the development of the macrodomain strength in addition to compaction as a physical process and H-bonding by the residual water molecules, some of which will occupy pore space in the macrodomains.

Victorian brown coals can be fractionated into Solvent
Soluble Extracts (SSE), Humic Acids (HA) and a Kerogen (K) residue (6). These are lithotype dependent in concentration hence ROM coals will be variable also in the relative composition of functional groups reactive in densification. SSE have high H/C ratios (7) but do contain some acidic components. These latter could be involved in domain development but on first principles HA and K fractions may be expected to provide good substrates for cross-linking. Indeed humic acids have been implicated in the formation of Solar Dried Coal (8). In our tests neither HA or K additives enhanced the crush strengths derived from LY DBC. The complication of pH, as yet unresolved, clouds the interpretation however, since HA additives are acidic in nature and lower the pH of the raw coal feed. Low pH coals do not develop a significant crush strength in general, nor in the particular, as shown in Table 2 for Loy Yang coal.

Table 2. Effects of Kerogen and Humic Acid Additives on Densification.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Additive</th>
<th>pH</th>
<th>Crush Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loy Yang ROM</td>
<td>None</td>
<td>3.9</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>25% Kerogen</td>
<td>4.3</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>NaHCO₃</td>
<td>4.9</td>
<td>16.1</td>
</tr>
<tr>
<td></td>
<td>20% Humin acid</td>
<td>3.5</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>20% HA + NaOH</td>
<td>5.9</td>
<td>18.1</td>
</tr>
</tbody>
</table>

Densification offers an advantage in that it readily allows the formation of a moulded coal but importantly the gross characteristics of DBC are still those of the ROM coal (Table 2). Figure 7 exemplifies this well in that the pyrograms for Loy Yang ROM and DBC are very similar. Thermal desorption of brown coal at 350°C releases primarily triterpenoid components which are virtually lacking in the 600°C pyrogram. Thermal desorption of DBC with a base additive, however, gives a significantly lowered yield of triterpenoids and suggests that components can be chemically incorporated into the DBC by this process, once again implicating oxygenated functional groups in densification.

Acknowledgement.
The authors thank CRA - Advanced Mineral Chemistry for financial support.

References
5. For example, U.S. Patents 4,627,575 and 4,701,184.
FLOW CHART FOR DENSIFICATION

Run-of-mine brown coal, 60% water

- Lump
- hammer-mill
- -50mm
- attritioning kneader/extruder
- paste, -15 microns 60% water
- drying
- Densified Brown Coal 10-15% water

MOISTURE LOSS CURVES

Drying at 20°C and 50% rel. humid.

MOISTURE [%]

TIME (HOURS)

LOY YANG COAL

MORWELL COAL
FIGURE 6. TYPICAL pH EFFECTS ON CRUSH STRENGTH
ROLE OF PYRITE DURING THE THERMAL DEGRADATION OF KEROGEN USING IN-SITU HIGH TEMPERATURE ESR TECHNIQUE

By

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INTRODUCTION

Thermal maturation of kerogen in sedimentary rocks has been studied extensively with the intent of better understanding the generation and accumulation of oil and gas (1, 2). The influence of mineral matrices on kerogen during thermal maturation has also been studied. The available in literatures have shown that the role of catalysis in pyrolysis reactions have been directed towards using minerals, such as kaolinite, montmorillonite and calcite (3-7). Analytical techniques applied in these studies did not included in-situ ESR spectroscopy. Moreover, the relationship between pyrite and kerogen has received no attention considering a possible catalytic role of pyrite on the thermal degradation of kerogen. The genetic relationship between pyrite and kerogen, in addition to the evidence that pyrite whether indigenous or added, enhances coal conversion and improves product quality under hydrolquefaction conditions (8-11) makes one wonder whether pyrite also plays a role in kerogen maturation. In this work, in-situ ESR studies between room temperature and 700 °C on the pyrolysis of kerogen in the presence and absence of added pyrite
are reported.

EXPERIMENTAL

Samples studied here include lignin, natural and artificial kerogen. Lignin is a pure reagent supplied from Tokyo Kashei Kogyo. Natural kerogen samples were taken from the MITI-Hamayuchi borehole and Oashizawa outcrops in Japan. Artificial kerogen was prepared from a mixture of glucose and casein (12). Pyrite is a reagent supplied from CERAC, Inc., and was checked with X-ray diffraction and Mossbauer spectroscopy before use. Procedures of Kerogen demineralization and extraction with organic solvents, have been discussed previously (13). The procedure of in-situ high temperature ESR measurements of kerogens has been described elsewhere (14). Since pyrite cannot be fully removed without specific alteration of kerogen structure, no attempts have been made to remove pyrite from the natural kerogen under investigation. Therefore the role of the indigenous pyrite cannot be justified in this study, and discussion will be focused on the added pyrite. To check the catalytic effect of added pyrite on the formation of free radicals, lignin and artificial kerogen as pyrite free materials were tested with and without addition of pyrite.

RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of radical concentration for lignin with and without addition of pyrite. There are two significant points that should be mentioned:

(1) the maximum value of spin concentration for pyrite-lignin system is larger than that of the lignin one. (2) pyrite speeds up the process of radical formation, where the maximum value of spin concentration of the lignin-pyrite system is shifted significantly to lower temperature, from 575 °C to 550 °C.
In Fig. 2, the temperature dependence of radical concentration for artificial kerogen alone and the same kerogen with 10% FeS$_2$ is illustrated. The main effects of pyrite on the thermal decomposition of kerogen are manifested by:

1. A drastic enhancement in radical concentration that starts from 225 °C and proceeds throughout the course of pyrolysis. This enhancement becomes intensive at 450 °C (the temperature of $R_3$) and drops after that. 2. Speeding up the process of pyrolysis. This causes shift of the ESR maxima ($R_1$ and $R_3$) and ESR minimum ($R_2$) to lower temperatures. Lowering in temperatures was measured as 25 °C for both $R_1$ and $R_2$, and 50 °C for $R_3$.

Using the in-situ ESR technique, it has been shown that kerogen maturity and hydrocarbon generation are linked to an extent to that of free radicals therein (15). Fig. 3 demonstrates the temperature dependence of radical concentration for kerogen from Oashizawa outcrops with and without addition of pyrite (10% and 30% FeS$_2$). In the 10% FeS$_2$ system, enhancement of radical concentration starts at 275 °C and continues throughout pyrolysis. As for the 30% FeS$_2$ system, the observed enhancement of the radical concentration starts earlier at 200 °C and becomes more pronounced than that in 10% FeS$_2$. Pyrite accelerates the process of radical formation in kerogen. This is manifested by shifting the temperature of the maximum value of radical concentration to lower temperature when pyrite was added. The larger the amount of pyrite is used, the more the shift in the temperature of the ESR maximum can be observed. This shift in temperature follows the sequence kerogen-30% FeS$_2$ > kerogen-10% FeS$_2$ > kerogen.

Five kerogen samples from MITI-Hamayuchi borehole were mixed with 10 and 30% FeS$_2$ and examined by ESR. These samples ranges in
depth from 904 to 4499 meters, and covers the diagenesis and
beginning of catagenesis. The temperature dependence of radical
concentration for Hamayuchi kerogens in the presence and absence
of pyrite as an additive is shown in Figs. 4 and 5 for the
shallowest (No. 1) and deepest (No. 5) sample, respectively.

Pyrite in the diagenesis stage. This stage is represented by
two samples (Nos. 1 and 2). In sample No. 1 (Fig. 4), the free
radical concentration markedly increases in the presence of 10%
FeS$_2$ than in the case when kerogen was pyrolyzed without the
additive. When 30% FeS$_2$ was used, an incremental enhancement in
reactivity over the 10% FeS$_2$ was observed. The overall order of
activity in terms of increasing spin concentration is as follows:
kergen-30% FeS$_2$ system > kergen-10% FeS$_2$ system > kergen alone,
clearly indicating the strong effect of FeS$_2$ during the pyrolysis
of kerogen. Also speeding up the process of radical formation can
be observed as the temperature at the positions of the maximum
values of spin concentration is shifted to lower temperature when
pyrite was added. Similar results were obtained for sample No. 2.

Pyrite in the catagenesis stage. The beginning of catagenesis
is represented by three samples (Nos. 3, 4 and 5). Fig. 5 shows
the results of sample No. 5. There is no noticeable change in
spin concentration using 10% FeS$_2$, where the spin concentration
in kerogen alone fraction and kerogen-10% FeS$_2$ one is nearly the
same. However, slight increase in spin concentration was observed
in the presence of 30% FeS$_2$ as is shown in Fig. 5 for sample No.
5. This results provide evidence that the effect of pyrite in
this stage is either small (for 30% FeS$_2$ system) or negligible
(for 10% FeS$_2$ system) comparing with the diagenesis stage.
Similar results were obtained for samples Nos. 3 and 4.

Decomposition of indigenous pyrite in kerogen. Three sets of
heating experiments were carried out on kerogen sample No. 1. at 325, 375 and 450 °C in N₂ atmosphere. X-ray diffraction and Mossbauer showed transformation of indigenous pyrite to pyrrhotite at 450 °C.

Decomposition of reagent pyrite. Five sets of experiments have been conducted in N₂ atmosphere at 250, 375, 425, 475 and 550 °C. The transformation of pyrite to pyrrhotite was commenced at 250°C. This transformation process becomes more significant as the temperature increases to 550 °C. Thus it is evident that the large enhancement in radical concentration observed in the lignin-pyrite system (Fig. 1), artificial kerogen-pyrite system (Fig. 2) and natural kerogen-pyrite systems (Figs. 3 and 4) is consistent with the conversion of pyrite to pyrrhotite. The increase in radical concentration with FeS₂, may be attributed to the nascent sulfur produced during the process of conversion of pyrite to pyrrhotite. The pyritic sulfur is a strong hydrogen acceptor, where it may abstracts hydrogen from kerogen via a free radical process. This process of radical formation may take place as follows:

FeS₂ ←→ Feₙ₋₁S + S
pyrite pyrrhotite
S + RH ←→ HS⁻ + R
HS⁻ + RH ←→ H₂S + R⁺ (R= kerogen)

The enhancement of free radical formation via hydrogen transfer from kerogen (as a hydrogen donor) to sulfur (as a hydrogen acceptor) is illustrated in Fig. 6. Clearly, S is acting as a catalyst for generation of radicals in kerogen at these conditions. It should be noted that similar enhancement of radical formation by the catalytic effect of pyritic sulfur have been observed for coal (15).
Hydrocarbon generation and the role of pyrite. Hydrogen and carbon atoms crack from kerogen to form petroleum. This cracking process proceeds via free radicals formation. The more hydrogen a kerogen contains, the more hydrocarbon it can yield during cracking, and the more activity of pyrite can be observed. With increasing burial depth in Hamayuchi samples, the aliphatic hydrocarbons decrease. FT-IR data shows that the intensity of the aliphatic portion of kerogen carbon (CH) between 3000-2700 cm^{-1} in sample No.1 is larger than that in sample No. 5. Elemental analysis also shows that sample No. 1 is richer in hydrogen than sample No.5. This may be the reason responsible for the activity of pyrite in sample No. 1.

CONCLUSION

Based on the data presented in this study, pyrite acts indirectly as a catalytic agent via sulfur. Pyritic sulfur enhances the formation of free radicals which may reflect enhancement in the hydrocarbon generation.
Figure 3. The temperature dependence of radical concentration of Oashizawa kerogen in the presence and absence of FeS₂.

Figure 4. The temperature dependence of radical concentration of Hamayuchi kerogen No.1 in the presence and absence of FeS₂.

Figure 5. The temperature dependence of radical concentration of Hamayuchi kerogen No.5 in the presence and absence of FeS₂.

Figure 6. The temperature dependence of radical concentration of artificial kerogen in the presence and absence of sulfur.
LITERATURE CITED


Minerals and Inorganics Associated with South Australian Lignites

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The Levels, South Australia 5095, Australia

INTRODUCTION

South Australia is endowed with considerable reserves of low rank Permian to Jurassic sub-bituminous coal and Tertiary lignite. A number of these occurrences have been evaluated since the mid 1970's to assess their suitability for power generation. Of the lignites, the Bowmans (1,600 Mt) and Lochiel (580 Mt) deposits from the Northern St. Vincent Basin have been the subject of extensive research. Both these lignites contain in excess of 50% moisture and very high Na, Cl, and S contents, all of which create problems for any subsequent utilization. Combustion trials on both Bowmans and Lochiel lignites have been conducted as well as pilot scale gasification and circulating fluidized bed combustion tests. As a consequence of this work it has been realised that the non-carbonaceous component of the lignite presents major technical and economic problems.

In the light of this, an extensive research program has been conducted at the S.A. Institute of Technology to determine both the minerals and inorganics present and their distribution in South Australian lignites. A major part of this project was the development of techniques to enable the analysis of minerals using Scanning Electron Microscopy (SEM) with Back Scattered Electron (BSE) imaging, Energy Dispersive X-Ray Spectrography (EDS), X-Ray Diffraction (XRD) and mechanical dewatering to extract water for subsequent analysis.

LITERATURE REVIEW

The occurrence of non-carbonaceous material in coals has been the subject of much research, especially in relation to its effect on utilization and ash formation ((1)-(7)). In contrast to high rank coals where the coal mineral matter represents the total non-carbonaceous fraction, the low rank coals have two categories of non-carbonaceous material: minerals (discrete particles e.g. quartz, marcasite, clays, etc) and inorganics (water soluble salts and exchangeable ions e.g. NaCl, Na2SO4, Al3+, etc) ((8), (9)).

Much of the literature published on minerals is based on high rank coals, but can be related to low rank coals ((10)). In general, the silicate minerals represent the major component of the minerals contained in coal. The most common analytical methods for mineral characterisation and analysis are listed in Harvey and Ruch (11) and covered in detail in the "Analytical Methods for Coal and Coal Products" series (12).

The majority of the early studies on inorganics was based on the determination of the chloride content, its mode of occurrence, and why it was present (13). It is only in more recent years with the increase in low rank coal utilization where the inorganics have a considerable economic impact that detailed research on inorganics has been undertaken ((9), ((14)-(17)). This work indicates that the inorganics in low rank coals exist in two forms: as free ions present in the water associated with the coal and as cations exchanged on to the surface functional groups of the coal. Analysis of the inorganics is most commonly done using leaching to extract the inorganics, followed by Atomic Absorption techniques for cations and standard chemical analysis for anions.
Samples

Typical analyses of the four South Australian lignites are given in Table 1. They are ranked as Lignite B on the ASTM system.

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>Bowmans</th>
<th>Lochiel</th>
<th>Sedan</th>
<th>Kingston</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>56</td>
<td>61</td>
<td>59</td>
<td>53</td>
</tr>
<tr>
<td>Higher Heat Value (wet basis)(MJ/kg)</td>
<td>10.6</td>
<td>9.1</td>
<td>9.1</td>
<td>10.6</td>
</tr>
<tr>
<td>% Ash (db)</td>
<td>14</td>
<td>16</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>% Vol. Matter (db)</td>
<td>46.7</td>
<td>49.9</td>
<td>43.9</td>
<td>46.9</td>
</tr>
<tr>
<td>% Sulphur (db)</td>
<td>5.0</td>
<td>2.8</td>
<td>5.5</td>
<td>2.9</td>
</tr>
<tr>
<td>% Sodium (db)</td>
<td>1.55</td>
<td>0.95</td>
<td>0.60</td>
<td>0.85</td>
</tr>
<tr>
<td>% Chlorine (db)</td>
<td>1.5</td>
<td>0.5</td>
<td>0.25</td>
<td>0.15</td>
</tr>
<tr>
<td>% C</td>
<td>59.7</td>
<td>57.8</td>
<td>54.7</td>
<td>59.2</td>
</tr>
<tr>
<td>% H</td>
<td>3.9</td>
<td>4.7</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>% N</td>
<td>0.4</td>
<td>0.6</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>% O</td>
<td>17.0</td>
<td>18.2</td>
<td>15.0</td>
<td>18.3</td>
</tr>
</tbody>
</table>

* Data from the Electricity Trust of South Australia

TECHNIQUES USED IN THIS STUDY

SEM-BSE /SEM-EDS

A Cambridge Stereoscan 100 Scanning Electron Microscope with a KEVEX Energy Dispersive Spectrography unit was used in all the experimental work. In order to ensure optimum conditions for the analysis, it was necessary for the lignite samples to be in the form of a polished section. Lignite samples were crushed to all passing 2mm and allowed to air equilibrate at 20°C for 2 days. These partially dried samples were then impregnated with epoxy resin. After the resin had set, each sample was polished using diamond paste and kerosene as a lubricant. Prior to viewing under the SEM, each polished section was coated with a fine layer of amorphous carbon using a vacuum arc coater to ensure adequate electrical conductivity to prevent charging.

To enable detection of fine mineral particles, (<20μm) back-scattered electron imaging was used. Once the minerals were detected, the EDS was used for analysis. Selected lignite particles were scanned to determine the distribution of minerals. Mineral types were then differentiated by variation in back scatter intensity and identified using the EDS. The relative proportions (major, minor) and size distributions of the minerals were recorded. The overall surface of the polished section was viewed and "massive" minerals were analyzed and their distribution and size recorded.

Inorganic analysis was conducted in conjunction with the mineral analysis. Particles analyzed previously for mineral content were analyzed for their inorganic content, and an overall analysis conducted. The resultant EDS spectra output was fed into a spreadsheet software package which was adapted by the authors to allow the calculation of a quantitative elemental analysis.
X-Ray Diffraction

Lignite samples were predried at 105°C for 2 hours to remove the water which is a major impurity component, hence its removal in effect concentrates the mineral species. After drying, the samples were crushed using a mortar and pestle until all passing 75μm. The dried lignite powder was then mounted in a standard aluminium mounting plate and placed in a Philips X-ray Diffractometer with a Rigaku power source. A Co X-ray tube was used to suppress fluorescence of any elemental species. The resultant diffraction pattern was resolved using the JCPDS Fink and Hanawalt Indexes.

Leaching

Standard procedures using leaching for determining inorganic species in low rank coals are well established. The procedures adopted for this study are given below. All lignite samples were crushed finer than 1mm and dried at 105°C for 2 hours. Samples weighing 2g were mixed with 100ml of distilled water and agitated for 1 hour. The resultant slurry was filtered and analyzed. The amounts of water soluble inorganics were calculated on a dry coal basis. For the acid extraction, 100ml distilled water and 15ml concentrated A.R. nitric acid were added, and the slurry boiled and simmered for 1 hour on a hot plate. The resultant slurry was filtered and analyzed to allow total inorganics present in the sample to be calculated.

Mechanical Dewatering

The analysis of water soluble inorganics present in the lignites can be calculated from the analysis of water contacted with the lignite as described above. It is uncertain whether water leaching induces any chemical charges (e.g. dissociation of ions from the surfaces of lignite or minerals, etc.). It was therefore considered that a more appropriate means of determining the analysis of water soluble inorganics would be to remove the water from the lignite by mechanical means. Design of equipment capable of mechanically dewatering lignites was obtained from the Grank Forks Energy Technology Centre and CSIRO. Using these designs as a basis, a mechanical press was constructed. The basic criterion for design was that it would dewater a sufficiently large sample of lignite to obtain a suitable volume of water for subsequent analysis.

All the lignite samples were initially crushed to pass 1mm and contact with the atmosphere was kept to a minimum. A lignite sample was placed in the die. The punch (which transfers the pressure from the Avery machine to the lignite) was then placed in the die. The lignite was then pressed against a series of water permeable screens and drainage plates. Under the applied pressure, water was expressed from the lignite sample and exited the dewatering device via the screens and drainage plates, whilst the dewatered lignite was retained on the screens. The expressed water was analyzed by conventional means.

RESULTS

The inorganics content of the lignite samples is given in Table 2 with the minerals and their distribution given in Table 3.
Table 2. Extractable Inorganics

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>EXTn</th>
<th>COMPOSITION (% db)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Ca</td>
</tr>
<tr>
<td>Bowmans</td>
<td>Acid</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>Press</td>
<td>0.93</td>
</tr>
<tr>
<td>Lochiel 1</td>
<td>Acid</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>Press</td>
<td>0.82</td>
</tr>
<tr>
<td>Sedan</td>
<td>Acid</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Press</td>
<td>0.23</td>
</tr>
<tr>
<td>Kingston 1</td>
<td>Acid</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Acid - acid extractable inorganics
Water - water extractable inorganics
Press - inorganics removed by mechanical dewatering.

Table 3. Minerals and Distribution in Lignite Samples

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>DISTn</th>
<th>DISTn DENSITY</th>
<th>MINERAL SPECIES</th>
<th>Major Size Range (µm)</th>
<th>Minor Size Range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOWMANS</td>
<td>-2+0.21mm medium even</td>
<td>Si</td>
<td>-500</td>
<td>CaS</td>
<td>-200</td>
</tr>
<tr>
<td></td>
<td>-0.21mm medium uneven</td>
<td>Al, Si</td>
<td>-500</td>
<td>Fe, S</td>
<td>-200</td>
</tr>
<tr>
<td>LOCHIEL 1</td>
<td>-2+0.21mm low uneven</td>
<td>Si</td>
<td>-500</td>
<td>Fe, S</td>
<td>-200</td>
</tr>
<tr>
<td></td>
<td>-0.21mm low uneven</td>
<td>Si</td>
<td>-200</td>
<td>Fe, S</td>
<td>-100</td>
</tr>
<tr>
<td>LOCHIEL 2</td>
<td>-2+0.21mm medium even</td>
<td>Al, Si</td>
<td>-200</td>
<td>Fe, S</td>
<td>-200</td>
</tr>
<tr>
<td>KINGSTON 1</td>
<td>-2+0.21mm medium even</td>
<td>Si (acic)</td>
<td>-20</td>
<td>Ca, S</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>-0.21mm low uneven</td>
<td>Al, Si</td>
<td>-200</td>
<td>Na, Al, Si</td>
<td>-150</td>
</tr>
</tbody>
</table>

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KINGSTON 2
-2+0.21mm medium uneven
  Si (acic) -20 Na,Al,Si -200
  Al, Si -500 Fe, S -200
  Ca, S -20

SEDAN
-2+0.21mm low even
  Si -500 Ca, S -500
  Fe, S -500
  Al, Si -50

-0.21mm medium uneven
  Ca, S -200 Fe, S -200
  Si -150
  Al, Si -150

Key to Table 3

<table>
<thead>
<tr>
<th>Elements detected</th>
<th>Species</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>quartz</td>
<td>SiO₂*</td>
</tr>
<tr>
<td>Si (acic)</td>
<td>acicular quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Fe, S</td>
<td>marcasite</td>
<td>FeS₂*</td>
</tr>
<tr>
<td>Ca, S</td>
<td>gypsum</td>
<td>CaSO₄.2H₂O*</td>
</tr>
<tr>
<td>NaCl</td>
<td>halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Al, Si</td>
<td>kaolinite</td>
<td>Al₂O₃.2SiO₂.2H₂O*</td>
</tr>
<tr>
<td>Na, Al, Si</td>
<td>plagioclase</td>
<td>Na₂O.Al₂O₃.6SiO₂</td>
</tr>
</tbody>
</table>

* elements detected using XRD

DISCUSSION

Analytical Techniques

The procedures developed for the analysis of the minerals and inorganics were the result of an extensive series of scouting tests to determine the optimum conditions for these specific sample types. This was then combined with general procedures for the analytical equipment (i.e. SEM-EDS and XRD units).

SEM-EDS

The equipment and procedure used had several inherent problems including:

1. Poor sensitivity of the EDS for elements of low atomic number (especially Na and Mg) and an inability to detect elements with atomic numbers less than 10. The software can derive quantitative analysis from a spectrum taking into account the inherent insensitivity of the EDS to those elements whose atomic numbers approach the detection limit.
2. The detection difficulties were then accentuated by the characteristic background x-ray spectrum which was superimposed on the x-ray spectrum of interest. This was overcome by the modelling and subtraction of the background from the acquired x-ray spectrum.
3. Preliminary tests indicated that the distribution of inorganics within a particle could be a function of the rate at which the lignite sample was dried. Rapid drying rates resulted in a concentration of inorganics in the central zone of a particle, whereas slow drying rates resulted in a concentration at the outer perimeter of the particle.
4. To enable quantitative analysis of the inorganics it is necessary to have a known standard. Chemical analysis of the sample to determine the concentration of one species i.e. Cl or S etc. will give a suitable standard.
5. The analysis does not distinguish between minerals and inorganics in the lignite. Despite these drawbacks, it was possible to detect trends occurring in the inorganics associated with the lignite.

The technique of BSE images on the SEM screen was ideal for the detection of minerals in low rank coals. The difference in atomic number between the major components of the coal matrix (i.e. C, H, N and O) and the elements present in the mineral species (i.e. Si, Al, Fe, Ca) means that the minerals fluoresce against the dark coal background. Variations in the BSE intensity between minerals was such that the different minerals present were also detectable. Using this technique, however, does in some cases make it difficult to differentiate between quartz and clay (kaolinite) just from a BSE image.

This problem can be overcome to an extent by differentiating between the actual crystal structure which is apparent between quartz, clay and other minerals. A secondary problem occurs as the low density of the coal matrix allows for a beam penetration to a depth of approximately 10μm. This means that the BSE image represents a surface volume rather than just a plane. Minerals which are subsurface are therefore visible, however there intensity is diminished (e.g. subsurface marcasite can have a similar BSE intensity to clay on the surface).

Analysis of the minerals detected using SEM-EDS was effective with simple minerals, however, determination of clay types was difficult and it was not possible to determine whether a mineral species was anhydrous or hydrated.

XRD

The limitation of an SEM-EDS analysis of minerals is that it cannot characterise the crystal structure of the minerals present. As a result it is difficult to determine some mineral types i.e.

1. differentiating clay types
2. whether the presence of Fe and S is indicative of pyrite, marcasite or FeSO₄.
3. minerals which have anhydrous and hydrated forms.

XRD allows the determination of the actual mineral species present. The bulk coal samples resulted in an x-ray pattern with a high background due to the coal matrix. The major mineral species were easily determined however, the minor species could not be detected. As with the SEM-BSE analysis, interpretation of results in a quantitative manner (in relation to the coal) is difficult. The major mineral species detected were quartz, kaolinite, gypsum (CaSO₄.2H₂O) and marcasite (FeS₂).

Minor mineral species were not detected as their concentration in the samples was below the detection limits for XRD.

Leaching

The limitation of water leaching is that some species which are not soluble within the coal sample may dissociate on leaching. For the acid leaching, a major problem arises from the dissolution of mineral species. This means that both cations exchanged onto the surface are removed as well as ions from the minerals and it is not possible to determine the amount of ions related to the two different environments.

Mechanical Dewatering

The design of the mechanical dewatering press is such that there is a limit to the pressure under which the lignite is subjected. The dewatering pressure is one of the major factors determining the extraction of water, and a suitable sample of mechanically removed water
could not be obtained from the Kingston sample. Overall the technique was successful and several good water samples were obtained from the Bowmans, Lochiel and Sedan samples.

**Data Obtained on South Australian Lignites**

**Inorganics**

The inorganics analysis given in Table 2 show that all of the South Australian lignites have high Na, Cl and S contents. The Bowmans lignite has the highest Na and Cl levels of 1.86% and 1.98% respectively.

In general the water soluble inorganics consist of predominantly Na, Cl and S (as SO₄²⁻) with lesser amounts of Ca and Mg. The Bowmans and Lochiel lignites, both from the St. Vincents Basin, have very high Na, Cl and S as a consequence of the saline environment in this region. The Sedan lignite in contrast has very high Ca and Mg concentrations (1.3 and 1.19% respectively). The Kingston lignite exhibits a relatively low concentration of water soluble inorganics.

Acid leaching results give an indication of the total inorganics present in the coals, including:

- water soluble ions;
- cations exchanged onto the surface functional groups associated with the coal;
- cations exchanged onto the clay minerals
- ions emanating from the dissolution of hydrolysis of minerals.

The water soluble component is easily differentiated, however the other three are not. For the Bowmans, Lochiel and Sedan lignites the acid soluble components (i.e. total inorganics - water soluble inorganics) are predominantly cations (Na, Mg, Ca, Al and Fe) which are exchanged onto the lignite surface. In contrast, for Kingston lignite which has the highest acid soluble component, inorganics are (compared with the water soluble component) associated with ions associated with or exchanged in the clay minerals.

Analysis of the mechanically removed water showed some significant variations especially with respect to Na. It can be seen that for Bowmans, Lochiel and Sedan lignites, the Na content detected by mechanical removal of water is noticeably less than that for the water soluble Na. This aspect of the occurrence and distribution of Na (and Cl) within these samples was discussed in detail in a paper presented by the authors recently (17). The distribution of Na was found to be a function of the high negative surface charge of the coal surface resulting in adsorption of Na at this surface.

**Minerals**

All of the samples analysed showed, as expected, that the major mineral species were quartz and kaolinite (syngenetic), marcasite and gypsum (epigenetic). In general the quartz was present in two distinct size ranges: 500μm and 50μm.

One major variation was noted in the two Kingston samples where the majority of the quartz was acicular in form and -20μm in size. The size distribution of the kaolinite was quite variable and again the Kingston sample differed in that most of the kaolinite had Na associated with it. Marcasite was commonly present as an intimately associated impurity within the coal and in many cases it had replaced the original coal structure (psuedomorphing). The gypsum was present mainly in the -20μm size range. Overall the mineral matter content of the lignites was in the order of 5-10% (i.e. a medium distribution density).
SUMMARY AND CONCLUSIONS

Minerals and inorganics from the South Australian lignite deposits have been determined using both standard and specifically developed analytical techniques. Techniques used include SEM-BSE/SEM-EDS, XRD, leaching and mechanical dewatering. The inorganics within the lignite samples showed variations between deposits and within the same deposit. Quartz and kaolinite were the predominant mineral species and these also exhibited major variations within and between deposits.

ACKNOWLEDGEMENT

This research was financed by the South Australian State Energy Research Advisory Committee (SENRAC).

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ASSOCIATION OF MINERAL MATTER WITH THE ORGANIC COAL MATRIX

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Iowa State University, Ames, IA 50011.

ABSTRACT

Advances in the quantitative assessment of the association of mineral particles with the organic coal matrix have been made recently at the Ames Laboratory. In addition to routine analysis of mineral matter for particle size and mineral phase, coal particles are classified according to the mass fraction of the various minerals found in cross sections of the particles. Particles are also classified according to the relative amount of mineral matter and coal present on their surface. Examples are given of the resulting distributions for individual minerals showing their liberation, and results are related to coal recovery and ash reduction of the sample during cleaning.

INTRODUCTION

Variations in the characteristics of mineral matter in coal have a significant bearing on the effectiveness of removal of mineral matter during cleaning. The size distributions of the mineral particles play a significant role in determining cleanability since it is generally easier to remove the larger mineral particles. However, it is the association of mineral particles with the organic coal matrix that ultimately determines the cleaning potential. On occasion, certain minerals can be preferentially liberated and then physically removed while others remain associated with the coal matrix.

In practice, coal is not ground to a size at which all mineral matter is liberated from coal; it would not be economically feasible. Rather, coal is processed only to the extent that is necessary to comply with applicable environmental regulations. In this context, it is more important to know to what extent the coal and minerals are still associated.

In the last few years, image analysis techniques have been adapted to the in-situ characterization of the association of individual minerals with coal. Scanning electron microscopy (SEM) is used to observe coal and mineral particles in cross section, energy-dispersive x-ray analysis (EDX) is used to determine the elemental composition of the mineral particles, and automated image analysis (AIA) is employed to characterize a sufficient number of particles for reproducibility. Such techniques have been in use in the mineral industry for many years (1,2). However, the application of these techniques to coal has lagged, partly due to the inability to resolve coal particles from the mounting media. Conventional epoxy resins do not exhibit contrast with coal particles. Therefore, the use of carnauba wax was developed as an alternative and effective medium (3).

METHODOLOGY

Two sets of coal samples were chosen to illustrate applications of AIA to coal processing. The first coal was a 200-mesh sample of Williams Fork 0 bed coal from Moffat County, Colorado. The coal is ranked as sub-
bituminous A, with 15.3% moisture, 4.18% ash, and 0.45% total sulfur. The coal was subjected to bench-scale float-sink cleaning at 1.6 sp.gr. in a centrifuge. Samples of the raw coal and the float and sink fractions were then collected for analysis. The full procedure has been described extensively elsewhere (4). The second sample was a 325-mesh sample of Upper Freeport coal with 1.3% moisture, 9.88% ash, and 1.36% total sulfur. The coal was cleaned in two separate tests by float-sink and by froth flotation, as described elsewhere (5). Only samples of the raw coal were available for AIA.

Coal samples with their included mineral matter were prepared for image analysis by mixing samples of the dry coal with polyethylene powder (as a diluent) and molten carnauba wax. Because SEM-AIA is often used to explain behavior under a specific set of processing conditions, samples are typically prepared in the same size in which they are received. Pellets were then cut to expose a vertical cross section and polished using standard petrographic procedures. They were then coated with 150 Å of carbon to provide a conductive surface.

Samples were examined with an electron beam of 15 keV and 0.7 nA at magnifications of 200-500 using the backscattered electron (BSE) signal. Use of the BSE signal permits relatively easy differentiation of minerals and coal from each other and from the carnauba wax using simple brightness thresholds. Coal and mineral particles were characterized for area and perimeter, and information on the relationship of adjoining particles with each other was preserved in the stored data. The amount of surface for each particle in contact with coal, mineral matter, and/or mounting media was recorded. X-ray spectra were then collected for 4 seconds for each of the mineral particles. The integrated intensities for 20 elements were compared with a previously prepared table listing ranges of elemental intensities characteristic of minerals found in coal in order to identify the particles (6,7). Handbook values of mineral densities were then used to convert the results from area fractions to weight fractions, which are of more direct interest in coal preparation.

Results involve very detailed information for the composite coal/mineral particles and their component parts (i.e., size, identification, and surface associations). The analyst can then prepare tables showing the distributions of the sample mass as a function of the appropriate characteristic. These distributions can then be related to processing behavior. Examples of such distributions are given below.

RESULTS AND DISCUSSION

A typical distribution of mineral matter according to particle size and mineral phase is given in Figure 1 for the major phases in the raw sample of Williams Fork coal. Such particle size distributions relative to the size of the coal particles can be used to predict the ash reduction potential, since larger mineral particles are generally more easily removed, while small mineral particles are likely to be associated with the organic matrix and to appear with the clean coal product. As seen in Figure 1, most of the mineral matter in this coal is quite fine and is thus expected to be rather difficult to remove. However, it is not unusual to find minerals, such as those that occur as cleat fillings, that are readily liberated and then removed by cleaning. Such is also the case with the pyrite in this coal. Pyrite particles show a bimodal size distribution in Figure 1. The larger particles are likely candidates for
removal; however, analysis of the 1.6 sp.gr. float fraction of the coal shows that even small grains of pyrite were removed, implying that they were very well liberated. Such cases point out the need to perform some form of association analysis in order to better characterize the coal.

As one alternative, we have chosen to express the coal–mineral association results in terms of the weight fraction of mineral matter in the particle, as determined from the cross section. This corresponds with the so-called grade distributions used in the mineral industry (1,2). Such a distribution for the same sample of Williams Fork coal is shown in Table 1. The results can also be plotted as done in Figure 2 to show the amount of sample of the indicated grade. Samples with good liberation of minerals from coal show a wide separation between coal-rich material on the left and mineral-rich material on the right side of the figure. In this sample there is much mineral matter found across the entire range of grades, indicating that liberation of mineral matter is not complete at this particle size, and that physical cleaning would therefore be difficult.

The cumulative amount of coal and associated mineral matter, observed in Figure 2, can be used to estimate coal recovery and its anticipated ash content during a density-based separation. However, such a correlation is complicated since the AIA-observed mineral content does not directly reflect particle density. Still, such distributions often show dramatic differences between various coal samples. Similar figures for float or sink fractions can reveal the misplacement of coal- or mineral-rich particles to the wrong fraction so that improvements can be made in the process.
Table 1. Distribution of coal and mineral phases in raw Williams Fork coal as a function of particle mineral matter content.

<table>
<thead>
<tr>
<th>Range of Mineral Matter (%) in Particle</th>
<th>Coal % 0-9</th>
<th>10-19</th>
<th>20-29</th>
<th>30-39</th>
<th>40-49</th>
<th>50-59</th>
<th>60-69</th>
<th>70-79</th>
<th>80-89</th>
<th>90-99</th>
<th>100</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>0.11</td>
<td>0.10</td>
<td>0.19</td>
<td>0.28</td>
<td>0.38</td>
<td>0.54</td>
<td>0.64</td>
<td>2.26</td>
<td>5.36</td>
<td>28.61</td>
<td>54.36</td>
<td>93.03</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.39</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>Kaol.</td>
<td>0.07</td>
<td>0.09</td>
<td>0.11</td>
<td>0.13</td>
<td>0.06</td>
<td>0.10</td>
<td>0.05</td>
<td>0.08</td>
<td>0.06</td>
<td>0.06</td>
<td>0.00</td>
<td>0.81</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.23</td>
<td>0.16</td>
<td>0.20</td>
<td>0.03</td>
<td>0.08</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.00</td>
<td>0.76</td>
</tr>
<tr>
<td>Mont.</td>
<td>0.40</td>
<td>0.01</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.00</td>
<td>0.61</td>
</tr>
<tr>
<td>Other</td>
<td>1.77</td>
<td>0.39</td>
<td>0.16</td>
<td>0.32</td>
<td>0.28</td>
<td>0.21</td>
<td>0.23</td>
<td>0.32</td>
<td>0.37</td>
<td>0.34</td>
<td>0.00</td>
<td>4.38</td>
</tr>
<tr>
<td>Total</td>
<td>2.97</td>
<td>0.67</td>
<td>0.70</td>
<td>0.78</td>
<td>0.81</td>
<td>0.90</td>
<td>1.17</td>
<td>2.71</td>
<td>5.85</td>
<td>29.08</td>
<td>54.36</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 2. Distribution of coal and mineral matter in raw Williams Fork coal as a function of the particle mineral matter content.

The data of Table 1 can also be plotted for the individual minerals to show variations in the modes of their association, as shown in Figure 3. This figure dramatically shows the difference between pyrite and the other minerals in their association with coal. Pyrite is found exclusively in particles containing more than 80% mineral matter, while the other minerals are associated with particles containing a wide range of mineral matter. From this figure, it appears that pyrite should be easily removed during float-sink separation, which proved to be the case in actual separations, both on a laboratory scale (5) and in practice. Representatives from the mine which produces this coal confirmed that the pyrite occurs as cleat fillings and is rather easily removed (8). Similar
conclusions might be reached by routine manual observation of the polished sections or from operating experience; however, these AIA-SEM techniques permit the measurements to be quantified for comparisons among coals.

In addition to expressing coal-mineral association as a function of particle mineral matter content, as described above using the Williams Fork coal as an example, our recent efforts have emphasized determining association based on particle surfaces. While the previous distributions provide an indication of the probable cleaning behavior of a coal in a density-based process, they do not lend much insight into cleaning behavior during surface-based processes such as froth flotation or oil agglomeration. For such processes it would be better to have results expressed in terms of the proportion of coal (or minerals) present on the surface of the particles. If it were possible to relate floatability to the amount of coal on the surface, then it may be possible to relate cleanability to the AIA-SEM results.

Figures 4 and 5 show the coal-mineral association for Upper Freeport coal based on the mineral weight fraction and the mineral surface fraction of the particles. There is considerable difference between the two figures. While Figure 4 shows that about 74% of the mineral matter is present in particles containing more than 50% mineral matter (i.e., less than 50% coal), Figure 5 indicates that only 10% of the mineral matter is found in particles with less than 50% of the surface covered by coal. Indeed, about 75% of the mineral matter is found in particles with more than 80% coal on the surface. These results indicate that density-based processes (e.g., float-sink) should be able to remove significant amounts of mineral matter, while surface-based processes will likely be unable to
Figure 4. Distribution of coal and mineral matter in raw Upper Freeport coal as a function of particle mineral matter content.

Figure 5. Distribution of coal and mineral matter in raw Upper Freeport coal as a function of particle surface occupied by minerals.
significantly reduce mineral content. Results of cleaning tests reported elsewhere (5) verified these predictions. Float-sink separations at 1.6 sp.gr. reduced the ash content by 57% with a 90% recovery, while froth flotation for 3 minutes resulted in only a 16% reduction in ash content with about the same recovery. Although these AIA results are quite preliminary, they show a strong general correlation with actual cleaning behavior.

SUMMARY AND CONCLUSIONS

AIA-SEM provides insights into coal character and processing potential that are unavailable by other means. Many of the advantages of the technique stem from its ability to characterize coal and mineral particles, in-situ, on a microscopic level. Distributions of mineral matter as a function of particle size and mineral type are readily available and provide some indication of coal cleanability. Results are also now available showing the distribution of phases based on the weight fraction of mineral matter in the particle or based on the relative amount of surface of the particle occupied by mineral matter. These distributions can be related to processing behavior and can be used to explain, and possibly even predict, the recovery and quality of product under various cleaning conditions. The results are especially useful for detecting differences between various coals and for finding the reasons for unusual processing behaviors.

ACKNOWLEDGEMENT

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LITERATURE CITED


Despite considerable effort to understand the chemical nature of the organic and inorganic portions of coal, and substantial advances in instrumentation and methodologies, much of coal's chemical nature remains intractable. This paper reviews methods and their limitations for the determination of specific minerals in coal, and presents results of efforts at Consolidation Coal Company to develop FTIR methods for routine coal mineralogy.

Mineral matter characterization has received considerable attention. Given and Yarzab (1) discussed the problems posed by mineral matter in various coal analyses. Furthermore, mineral matter complicates the chemical treatment of coal. It also has many adverse effects on commercial coal utilization. Coal consumers pay to ship mineral matter, to accommodate its impact on capital equipment and operations, and to dispose of the resultant ash. The impact of coal minerals on utilization motivated Consol's initial interest in mineralogy (2).

The results reported here are from a second phase of the FTIR method development, in which extensive improvements were made to the methods.

EXPERIMENTAL

DESCRIPTION OF SAMPLES

Small Data Set. Low-temperature (plasma) ashes (LTAs) were obtained from ten diverse coal samples (Table 1), ranging in rank from lignite to Ivb. Infrared spectra were obtained of duplicate samples of each coal. A separate set of duplicates was generated for four of the coals.

Large Data Set. LTAs were analyzed by FTIR for 50 coals, ranging in rank from lignite to Ivb. These were a representative subset of duplicates of 95 unwashed and clean commercial coals from the eastern, midwestern and western U.S. and Alberta, Canada. The 50-coal set contained no duplicates, but different coal samples from the same mine were included.

Reference Minerals. The 42 reference minerals and the mineral classes used are listed in Table 2. Most of the minerals were obtained from Ward's Natural Science Establishment, Inc., Rochester, New York. Many of the silicate minerals were American Petroleum Institute (API) standard samples or their equivalents. Numbers given in the table (e.g., kaolinite 4) refer to the API standard designation.

METHODS

Coals ground to -60 mesh were low temperature (O2 plasma) ashed for about 100-125 hours for bituminous coals and 200 hours for lower rank coals. Ashing containers were made of Pyrex or ceramic.
Mineral standards were hand crushed to -1/4 inch, then ground to a fine powder in a ball or Bleuler mill. The powder was aerodynamically classified, and the finest fraction was collected. This was accepted as a mineral standard if 90% or more by weight was 5 µm and smaller particles. Duplicate 13 mm KBr pellets were prepared and the spectra were weight-scaled by reported techniques (3,4). With one exception, all the mineral standard spectra were averages of spectra from duplicate pellets.

LTA samples were ground for 30 minutes in a Wig-L-Bug (15 mg LTA, 50 mg KBr and 500 mg acetone in an agate vial), dried and stored in a dessicator. 13 mm KBr pellets were made and resulting spectra were weight-scaled (3,4).

All spectra were run on a Nicolet 7100 FTIR spectrometer equipped with a wide-band MCT detector. A Nicolet least-squares analysis program (MCOMP) was modified extensively for efficient use with a large number of reference minerals. The reference mineral with the lowest negative concentration was omitted upon each iteration, until only non-negative results were obtained. Generally 12 to 18 minerals remained in the final calculation.

For PLS or PCR calculations, the spectra were transferred to a DEC VAX 11/750 computer. The PLS and PCR program with cross-validation was provided by David Haaland of Sandia National Laboratory (3).

RESULTS AND DISCUSSION

A CRITIQUE OF METHODS FOR COAL MINERALOGY

This survey of five major methods for coal mineralogy and their limitations includes only methods which can provide a "complete" mineral analysis. Methods of limited applicability, such as Mossbauer, are omitted.

X-ray Diffraction. XRD is the most common method used for coal mineralogy (6,7,8). Its major advantage is the ability to unequivocally identify many minerals. The main disadvantages are: 1) reliance on reference minerals, 2) requires careful attention to sample preparation, and 3) low sensitivity to certain minerals (especially many clays) due to poor crystallinity and to particle orientation effects. Many laboratories analyze a separate concentrated clay fraction (less than 2 µm or 5 µm). However, sensitivity is still low and other limitations may arise: 1) the separated clay fraction may not be representative, and 2) the separation procedure can alter the sample. The original coal, instead of the LTA, can be analyzed by XRD. However, this is not satisfactory, since sensitivity is even lower. An extensive interlaboratory comparison of XRD results with Illinois 6 coal showed highly variable results (7). That study also included results from FTIR, SEM and other methods.

Infrared Spectroscopy. The use of IR (9,10,11,12) and FTIR (3,4) for coal mineralogy has been reported. Painter and coworkers (3) demonstrated that FTIR can provide a virtually complete analysis. Painter, Brown and Elliott (4), and others (9,10,11) discuss sample preparation, reference minerals, and data analysis. The advantages of IR are: 1) high sensitivity to molecular structure, 2) unequivocal identification of a number of minerals, 3) small sample size (a few milligrams), and 4) rapid analysis time (once LTA is available). Disadvantages include: 1) reliance on reference minerals, 2) requires careful attention to sample preparation, and 3) limited selectivity (discrimination among similar minerals).
The problem with limited selectivity includes some of the minerals which are problems for XRD: illite, muscovite, smectites and mixed-layer clays. Poor crystallinity creates problems with both XRD and FTIR. The IR spectrum of an amorphous material lacks sharp distinguishing features but retains spectral intensity in the regions typical of its composition. The X-ray diffraction pattern shows low intensity relative to well-defined crystalline structures. The major problem for IR is selectivity: for XRD it is sensitivity. In an inter-laboratory FTIR comparison (7), two laboratories gave similar results for kaolinite, calcite, and illite, but substantially different results for montmorillonite and quartz.

Electron Beam/X-ray Spectroscopy. Several methods based on point count or automated image analysis (AIA) in scanning electron microscopy-energy dispersive X-ray have been reported (13-18). Point count analysis can determine mineralogy; AIA can also determine the size distribution of the minerals. These methods obtain a point-by-point or particle-by-particle elemental analysis. A mineral distribution and analysis is obtained by classifying each elemental composition into one of the mineral categories. Such methods have several advantages: 1) they can be automated, 2) the composite elemental composition can be checked against that of the bulk sample, 3) it is possible to run coal (not necessary to obtain LTA), and 4) they provide some information on statistical and perhaps spatial, size, or morphological distribution of the minerals. For these reasons, such methods have become more popular in recent years. The major disadvantages are: 1) the chemical information and thus the selectivity is limited, since it uses only elemental composition, 2) it relies on a suitable classification scheme for mineral categories, and 3) data collection can be time-consuming (especially for AIA), requiring many hours per sample.

Optical Microscopy. Optical microscopy is the traditional tool of geologists and petrographers for mineral identification and characterization (19). It has two main advantages: 1) positive identification of minerals can be achieved, and 2) information is obtained on mineral distribution and morphology. However, quantitation is difficult, and the analysis is time-consuming, requires highly trained technicians, and is not amenable to automation. Although in common use in petrographic studies, such methods have been displaced by XRD, IR, and SEM-EDS methods for mineralogical studies.

Thermal Techniques. Thermal techniques, especially differential thermal analysis (DTA) have been used for mineral identification (19) and for coal mineralogy (20). The advantages of thermal techniques are: 1) small sample size, 2) little sample preparation (applicable to whole coals), 3) potentially rapid analysis, and 4) information relevant to combustion behavior may be provided. The disadvantages are: 1) the chemical information is limited, resulting in a lack of selectivity due to overlapping curves for individual minerals, 2) identification/quantification depends on reference minerals (though perhaps less sensitive to such problems than XRD or IR), and 3) it is not developed for quantitative use. Interpretation of thermal data is difficult, but could be improved by appropriate software. Variations, such as using different gases to highlight or suppress features, have been used (20). Detection limits of less than 1 wt % to about 30 wt % were reported for different minerals.

General Comments on Mineralogical Methods. The lack of a measure of quantitative accuracy is a general problem with mineralogy. A major limitation for XRD and IR methods is the use of reference minerals, and the standards used are from geological sources other than the coal analyzed. This limitation
will be avoided by only physical separation of the coal minerals or by data analysis techniques (such as factor analysis) which do not require reference minerals. Many studies have reported successful quantitation of mineral mixtures. This is a necessary, but not sufficient, criterion for a good mineralogical analysis. The differences between mineral mixtures and authentic samples are considerable, and good performance on real samples is not guaranteed. The major limitations of SEM-EDS and related techniques are appropriate classification of the elemental data, and obtaining a statistically sufficient number of data points. For classification of data, factor analysis, cluster analysis, or related multivariate techniques appear to be suitable.

The IR methods have progressed from hand-drawn baselines and peak height or area for quantitation, to spectral subtraction, to least-squares methods. Least-squares analysis eliminates the reliance on single peaks for quantitation and the subjectivity of spectral subtraction. However, negative concentration coefficients are a problem with least-squares analysis, since they have no physical meaning. Negative components can be omitted according to some criterion and the least-squares process iterated until only positive concentration coefficients remain. However, this does not ensure that the least-squares solution is a global minimum.

Haaland and coworkers [5] discussed other problems with classical least-squares (CLS) and its performance relative to partial least-squares (PLS) and factor analysis (in the form of principal component regression). One of the disadvantages of CLS is that interferences from overlapping spectra are not handled well, and all the components in a sample must be included for a good analysis. For a material such as coal LTA, this is a significant limitation.

Factor analysis extracts information from the sample data set (e.g., IR spectra) and does not rely on reference minerals. However, because abstract factors have no physical meaning, reference minerals may be needed in target transformations or other procedures to extract mineralogical information. One valuable piece of information obtainable without the use of extraneous data is the number of components required to represent the data within experimental error. Reported applications of factor analysis to mineralogy by FTIR are few [12]. However, one commercial laboratory is offering routine FTIR mineral analyses to the petroleum industry, based on related methods [22].

The next section of this paper describes the use of classical least-squares analysis of FTIR data to determine coal mineralogy. This is followed by promising preliminary results obtained using factor analysis techniques.

RESULTS USING CLASSICAL LEAST-SQUARES

Reproducibility. Mineralogical results from the ten-coal set (Table 3) are presented as ranges of values. In most cases, the reproducibility is good. Quartz, for example, shows consistently high reproducibility. However, illite, mixed-layer clays and montmorillonite in the first four coals show high variability. These minerals are similar in composition and spectral features. The variability in the FTIR results for these samples is related to variability in the spectral data. The set of ten duplicate spectra gave a pooled SD of 0.03 abs, while the separate set of four duplicate spectra gave a pooled SD of 0.08 abs. Results from the first four samples in the table included the poorer spectral data, while the results from the last six samples were obtained from the better spectra. The reproducibility for total clay content is good, even when vari-
ability in individual clay concentrations is high. Iron sulfides, oxides and sulfates also show some variability, particularly in the first and fourth samples.

Accuracy. Although there is no way to measure the accuracy of the FTIR mineralogical results, there are three areas in which it can be addressed (2,4). The first method is to compare pyrite results obtained by FTIR with the conventional ASTM determination. The agreement (Figure 1) is quite good over the range of 2.9 to 28.1 wt % pyrite in the LTAs from the ten coals. Similar results were obtained based on the 475-400 cm\(^{-1}\) region for a smaller sample set (2). The present results are based on the 1575-400 cm\(^{-1}\) range. The good agreement for the present data set is surprising, since the only spectral feature reported for pyrite in the mid-infrared is at ca. 415 cm\(^{-1}\). In these spectra, the noise level is high near 400 cm\(^{-1}\), and the identification of such a feature is not clear. It appears that the results are derived mainly from baseline curvature (resulting from the Christiansen effect). For all the iron sulfide minerals in the reference set, the baseline absorbance is near zero from ca. 1300 to 400 cm\(^{-1}\), but from 1300 cm\(^{-1}\) to 4000 cm\(^{-1}\) it curves upward.

The second method for indicating accuracy is to examine the spectral residuals from the least-squares fits (Figure 3, Table 4). The worst case was the lignite (coal SL), the large misfit at ca. 1380 cm\(^{-1}\) being due to the omission from the reference minerals of nitrate, presumably produced in the low-temperature asher by fixation of organic nitrogen (23). The reproducibility of the 28 original spectra (pooled SD) was 0.05 abs, slightly higher than the pooled standard fit error of 0.04 abs (without the lignite). However, the ten original duplicate spectra gave a pooled standard deviation of only 0.03 abs, which is slightly lower than the fit errors for most of these samples. In general, the fit error approached the experimental error in the original data.

The third method for assessing accuracy is to calculate an elemental composition for each LTA's oxidized ash, based on the reference mineral compositions. Reasonably close agreement between the actual and calculated elemental compositions would substantiate (but not prove) the mineral analysis. The standard error of prediction (SEP) for CaO, Fe\(_2\)O\(_3\), SiO\(_2\) and Al\(_2\)O\(_3\) (Table 4) ranged from 3.4 to 5.7 wt % for the various coals. The global SEP was 4.5 wt % for major ash element, the SEP values were 2.8 for CaO, 5.6 for Fe\(_2\)O\(_3\), 4.5 for SiO\(_2\) and 5.8 for Al\(_2\)O\(_3\). SEP values ranged from 0.3 to 5.7 wt % CaO, 2.3 to 10.3 wt % Fe\(_2\)O\(_3\), 0.1 to 11.6 wt % SiO\(_2\) and 3.0 to 5.6 wt % Al\(_2\)O\(_3\). Inspection of the elemental results also show some bias. CaO values were usually low, Fe\(_2\)O\(_3\) values were usually high, and Al\(_2\)O\(_3\) values were always low. Calcite impurities may be present in some of the reference spectra, or something else may interfere with the calcite. The high Fe\(_2\)O\(_3\) values, even though the pyrite values appear good, indicate that the determined iron oxides, sulfates, and/or siderite concentrations are too high. Somehow, certain iron minerals seem to be replacing or suppressing the appropriate aluminosilicates in the analysis.

In the next section, the potential for factor analysis and related chemometric techniques for providing improvements in the determination of minerals in coal by FTIR are explored.

RESULTS USING PRINCIPAL COMPONENT REGRESSION (PCR)

PCR is a technique in which principal component analysis (one form of factor analysis) of the spectra is followed by regression of the factor scores to calibrate and predict an independently-measured quantity. Besides the spectral
data, these calculations require other data. An accurate mineral analysis of each sample could be used to obtain a calibration. Because this is not possible, one is limited to modeling and predicting other measurable properties such as ash combustion behavior. It is possible to by-pass the mineralogy altogether, and model the desired properties or behavior directly from the LTA spectra. Ash property data which are readily accessible are ASTM ash fusion temperatures (reducing and oxidizing conditions) and ash elemental composition. PLS and PCR are linear models, but are capable of modeling some non-linearities (5). Ash elemental concentrations should be linearly related to intensities of bands in the infrared spectra (under ideal circumstances). Thus, PLS and PCR are expected to do a good job in modeling ash composition. However, ash fusion temperatures are not expected to be linearly related to spectral features.

Infrared data in the 1575-400 cm⁻¹ region (1218 points/spectrum) from LTAs from 50 coals (large data set) were used as input data to both PLS and PCR routines. This is the same spectral region used in the classical least-squares analysis of the small data set. Calibrations were developed for the eight ASTM ash fusion temperatures and the four major ash elements as oxides. The program uses PLS1 models, in which only one variable at a time is modeled. Cross-validation was used to select the optimum number of factors in the model. In this technique, a subset of the data (in this case five spectra) is omitted from the calibration, but predictions are made for it. The sum-of-squares residuals are computed from those samples left out. A new subset is then omitted, the first set is included in the new calibration, and additional residual errors are tallied. This process is repeated until predictions have been made and the errors summed for all 50 samples (in this case, 10 calibrations are made). This entire set of calculations is repeated once each time an additional factor is included in the model. The optimum number of factors is near the point at which the residual error reaches a minimum.

Results from these preliminary modeling efforts with the large data set are shown in Table 5. These results were obtained with centering (x and y) and scaling (x) as a data pretreatment. Only PCR results are shown, even though the PLS calculations took less computing time and gave slightly better results. The PCR model is preferred because it provides some additional information on our original data set. Results are depicted graphically in Figures 3 and 4 for the best and worst calibrations, respectively. The main measure of the success of these models is the SEP. For ash fusion temperatures, the SEPs were in the range of 50 to 78°F. The fusion temperatures at oxidizing conditions generally gave slightly better results than those at reducing conditions. These values represent errors somewhat larger than ASTM repeatability and reproducibility limits. The largest single prediction error for these models was about 200°F. This is no larger than the spread in interlaboratory results seen in round robin analyses of standard samples. Furthermore, these results appear to be equivalent to the best predictions of ash fusion temperatures available from ash elemental compositions (24,25,26). Many of those models have incorporated ratios, squared terms and log terms to get better results. It appears that the PLS and PCR models work reasonably well for modeling non-linearities in this case.

The PCR results for CaO, Fe₂O₃, SiO₂, and Al₂O₃ are quite good, as anticipated. The SEPs for CaO and Fe₂O₃ of 1.7-1.8 wt % are higher than the ASTM reproducibility limits, but the results for SiO₂ and Al₂O₃ are within the ASTM limits for those elements. Note that all these errors are better than the value of 4.8
resulting from the mineralogical analysis. (However, the mineral analysis was not optimized to predict ash elementals.)

The calibrations obtained are valid over a significant range of each property. It is feasible to predict all these properties from the LTA from a small sample of coal, should that be desired. These results mainly show that the methods employed can model other ash properties which are more closely related to large-scale combustion behavior. This is one area where further study is desirable.

Although the software used was not a full-featured factor analysis program, portions of the printed output are useful in studying the spectral data set. The table below shows some information obtainable from PCR models (large data set) with 5, 10 and 13 factors. In this case, the "factors" are principal components derived entirely from the sample data set. PLS factors are not interpretable in the same manner.

<table>
<thead>
<tr>
<th>No. of Factors</th>
<th>Prediction Residual Sum of Squares (Reconstruction of Original Data)</th>
<th>% of Total Spectral Variance of Data Set</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>89.9</td>
<td>93.5</td>
</tr>
<tr>
<td>10</td>
<td>28.1</td>
<td>98.0</td>
</tr>
<tr>
<td>13</td>
<td>11.5</td>
<td>99.2</td>
</tr>
</tbody>
</table>

An increase from 5 to 10 in the number of factors representing the original data results in a substantial reduction in the error. Because of the data pretreatment used, the spectral error cannot be directly compared to the experimental error determined from the data set. When five factors were used, two different lignite samples were flagged as possible outliers based on their spectral variances relative to the rest of the data set. With ten factors, one of the lignites was accommodated within the factor model (although ten factors may not have been required to accommodate it). With thirteen factors, both lignites were accommodated.

CONCLUSIONS

Experience in this laboratory has shown that even with careful attention to detail, determination of coal mineralogy by classical least-squares analysis of FTIR data may have several limitations. Factor analysis and related techniques have the potential to remove or lessen some of these limitations. Calibration models based on partial least-squares or principal component regression may allow prediction of useful properties or empirical behavior directly from FTIR spectra of low-temperature ashes. Wider application of these techniques to coal mineralogical studies is recommended.

REFERENCES

REFERENCES (Continued)


22. Harville, D. G. and Freeman, D. L., SPE Paper No. 18120 (1988), and phone conversations with the authors.


### TABLE 1

**DESCRIPTION OF COALS**

<table>
<thead>
<tr>
<th>Coals</th>
<th>Rank</th>
<th>Seam - Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>hvAb</td>
<td>Pittsburgh - Underground, Clean Coal, Greene Co., PA</td>
</tr>
<tr>
<td>EH</td>
<td>hvAb</td>
<td>Elkhorn 3 - Underground, Unwashed, Breathitt Co., KY</td>
</tr>
<tr>
<td>I1</td>
<td>hvBb</td>
<td>Illinois 5,6 - Surface, Clean Coal, Jackson Co., IL</td>
</tr>
<tr>
<td>SL</td>
<td>Lig</td>
<td>Scranton - Surface, Mercer Co., ND</td>
</tr>
<tr>
<td>I2</td>
<td>hvBb</td>
<td>Illinois 6 - Underground, Clean Coal, Jefferson Co., IL</td>
</tr>
<tr>
<td>I3</td>
<td>hvBb</td>
<td>Illinois 6 - Surface, Clean Coal Perry Co., IL</td>
</tr>
<tr>
<td>P2</td>
<td>hvAb</td>
<td>Pittsburgh - Underground, Clean Coal, Marshall Co., WV</td>
</tr>
<tr>
<td>P3</td>
<td>hvAb</td>
<td>Pittsburgh - Underground, Clean Coal, Monongalia Co., WV</td>
</tr>
<tr>
<td>GE</td>
<td>hvAb</td>
<td>No. 2 Gas, Upper and Middle Eagle - Underground, Clean Coal, Raleigh Co., WV</td>
</tr>
<tr>
<td>P0</td>
<td>lvb</td>
<td>Pocahontas 3 - Underground, Clean Coal, Buchanan Co., VA</td>
</tr>
</tbody>
</table>

### TABLE 2

**REFERENCE MINERALS**

**MAIN CLASSES**

- Kaolin - Kaolinite 4, 5, 6, Dickite 16, 27
- Mica - Biotite, Phlogopite, Muscovite
- Illite - Illite 36, Illite-Bearing Shale
- Mixed-Layer Clays - Metabentonite 37, 42
- Montmorillonite - 21, 22A, 22B, 24, 25, 26, 31
- Felspars - Albite, Anorthite, Orthoclase
- Chlorite - Chlorite
- Misc. AlSi - Attapulgite, Halloysite, Pyrophyllite 48
- Quartz - Quartz, Agate
- Fe sulfides - Marcasite, Commercial Pyrite, Mineral Pyrite, Pyrrhotite
- Fe oxides - Goethite, Hematite, Magnetite
- Fe sulfate - Difference spectrum weathered minus unweathered pyrite
- Siderite - Siderite
- Calcite - Calcite, Aragonite
- Gypsum - Gypsum, Drierite
- Dolomite - Dolomite

**GROUPED CLASSES**

- Clays - Kaolin, Illite, M. L. Clays, Montmorillonite, Misc. AlSi
- Other AlSi - Mica, Feldspar, Chlorite, Quartz
- Sulfate - Fe Sulfate, Gypsum
- Carbonate - Calcite, Siderite, Dolomite
- Fe Altered - Oxides, Sulfate

In addition to spectra of the 42 minerals shown above, the least-squares components included 3 "spectra" representing 1) moisture in KBr blank (obtained by subtraction of 2 KBr blank spectra), 2) a constant baseline offset (1 abs from 4000 to 400 cm⁻¹), and 3) a sloping linear baseline (line from 1 abs at 4000 cm⁻¹ to 0 abs at 400 cm⁻¹). Normalization of results used only the 42 mineral components, and disregarded these three components.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Pt (a)</th>
<th>EH (a)</th>
<th>11 (a)</th>
<th>SL (a)</th>
<th>12</th>
<th>13</th>
<th>P2</th>
<th>P3</th>
<th>GF</th>
<th>PO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koalin</td>
<td>25.8</td>
<td>33.9</td>
<td>11.8</td>
<td>16.6</td>
<td>15.1</td>
<td>21.8</td>
<td>1.1</td>
<td>2.9</td>
<td>23.2</td>
<td>25.7</td>
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<tr>
<td>Mica</td>
<td>2.6</td>
<td>6.4</td>
<td>2.9</td>
<td>9.3</td>
<td>0.0</td>
<td>3.3</td>
<td>0.0</td>
<td>-</td>
<td>7.6</td>
<td>10.5</td>
</tr>
<tr>
<td>Illite</td>
<td>7.1</td>
<td>13.6</td>
<td>20.2</td>
<td>33.8</td>
<td>3.7</td>
<td>47.4</td>
<td>0.0</td>
<td>1.2</td>
<td>20.8</td>
<td>25.1</td>
</tr>
<tr>
<td>Mixed Layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Clays</td>
<td>0.0</td>
<td>11.3</td>
<td>6.2</td>
<td>16.6</td>
<td>15.0</td>
<td>15.6</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>4.2</td>
<td>13.4</td>
<td>3.4</td>
<td>5.9</td>
<td>0.0</td>
<td>26.0</td>
<td>15.5</td>
<td>20.4</td>
<td>5.0</td>
<td>9.4</td>
</tr>
<tr>
<td>Feldspar</td>
<td>0.0</td>
<td>3.8</td>
<td>0.0</td>
<td>1.3</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>13.5**</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.6</td>
<td>2.5</td>
<td>3.4</td>
<td>4.9</td>
<td>0.0</td>
<td>2.3</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Misc. Clays</td>
<td>1.8</td>
<td>9.8</td>
<td>0.2</td>
<td>2.3</td>
<td>0.0</td>
<td>4.3**</td>
<td>0.0</td>
<td>2.7*</td>
<td>1.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>7.7</td>
<td>13.8</td>
<td>12.5</td>
<td>13.6</td>
<td>11.0</td>
<td>14.6</td>
<td>15.5</td>
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<td>14.8</td>
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<tr>
<td>Fe Sulfide</td>
<td>9.2</td>
<td>13.2</td>
<td>2.0</td>
<td>5.6</td>
<td>0.0</td>
<td>5.3</td>
<td>4.8</td>
<td>13.1</td>
<td>8.0</td>
<td>8.2</td>
</tr>
<tr>
<td>Fe Oxide</td>
<td>4.7</td>
<td>8.7</td>
<td>5.3</td>
<td>9.2</td>
<td>6.8</td>
<td>8.5</td>
<td>0.0</td>
<td>0.3*</td>
<td>5.5</td>
<td>7.3</td>
</tr>
<tr>
<td>Fe Sulfate</td>
<td>4.4</td>
<td>11.2</td>
<td>2.9</td>
<td>3.8</td>
<td>0.0</td>
<td>4.5</td>
<td>0.0</td>
<td>-</td>
<td>4.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Siderite</td>
<td>0.0</td>
<td>-</td>
<td>1.5</td>
<td>2.4</td>
<td>0.0</td>
<td>2.4</td>
<td>5.8</td>
<td>0.0</td>
<td>3.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.8*</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>0.5*</td>
<td>0.0</td>
<td>2.3**</td>
<td>3.4</td>
<td>49.2</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>-</td>
<td>0.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Alternate Classes

| Clays         | 54.0  | 60.0  | 55.3  | 59.7  | 67.7| 71.5| 19.6| 24.9| 56.4| 57.0| 36.9| 37.9| 37.7| 38.9| 39.4| 40.4| 53.7| 55.4| 47.8| 42.9|

Other Alumino

| Silicates     | 14.6  | 22.1  | 20.5  | 27.1  | 13.3| 17.2| 19.5| 34.4| 23.2| 24.8| 24.0| 24.1| 15.3| 15.5| 20.9| 22.1| 30.6| 32.5| 23.1| 25.3|
| Sulphates     | 4.4   | 11.2  | 3.2   | 3.8   | 2.3 | 5.0 | 34.4| 49.2| 4.3 | 5.2 | 9.0 | 9.3 | 14.8| 14.9| 10.8| 11.1| 1.0 | 1.8 | 1.6 | 1.7 |
| Carbonates    | 0.0   | -     | 1.5   | 2.4   | 0.0 | 2.8*| 2.4 | 5.8 | 0.0 | -   | 4.0 | 5.3 | 0.0 | -   | 0.7 | 1.1 | 0.0 | -   | 15.5| 16.0|
| Fe-Altered    | 9.3   | 20.0  | 8.2   | 12.4  | 7.5 | 13.0| 0.0 | 0.3*| 10.7| 11.6| 14.2| 14.6| 17.8| 17.8| 15.6| 16.8| 8.7 | 10.1| 9.3 | 10.5|

(a) Four samples run from each of these coals, two samples run from each of the remaining coals.

*One out of four samples gave a non-zero concentration.

**Two out of four samples gave a non-zero concentration.
### TABLE 4

**SPECTRAL FIT ERRORS AND ELEMENTAL PREDICTION ERRORS FROM FTIR MINERALOGY**

Spectral Fit Error (1575-400 cm\(^{-1}\)), Std. Dev. in abs.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>SEP Oxide wt % of Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.028</td>
<td>0.027</td>
<td>0.038</td>
<td>0.041</td>
<td>4.4</td>
</tr>
<tr>
<td>EH</td>
<td>0.030</td>
<td>0.033</td>
<td>0.023</td>
<td>0.029</td>
<td>4.3</td>
</tr>
<tr>
<td>I1</td>
<td>0.026</td>
<td>0.026</td>
<td>0.029</td>
<td>0.031</td>
<td>4.7</td>
</tr>
<tr>
<td>SL</td>
<td>-</td>
<td>0.250</td>
<td>0.149</td>
<td>0.194</td>
<td>4.1</td>
</tr>
<tr>
<td>I2</td>
<td>0.033</td>
<td>0.028</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I3</td>
<td>0.037</td>
<td>0.039</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>0.040</td>
<td>0.040</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>0.037</td>
<td>0.036</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CE</td>
<td>0.038</td>
<td>0.037</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P0</td>
<td>0.022</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With SL, pooled std. dev. = 0.093
Without SL, pooled std. dev. = 0.041

### TABLE 5

**PRINCIPAL COMPONENT REGRESSION CALIBRATIONS FOR SELECTED ASH PROPERTIES**

<table>
<thead>
<tr>
<th>Type</th>
<th>No. of Factors</th>
<th>SEP</th>
<th>Magnitude of Max. Prediction Error</th>
<th>Range of Input Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash Fusion Temperature, °F</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RID</td>
<td>5</td>
<td>72.4</td>
<td>169.9</td>
<td>1918 2757</td>
</tr>
<tr>
<td>RST</td>
<td>5</td>
<td>77.9</td>
<td>153.5</td>
<td>1972 2808</td>
</tr>
<tr>
<td>RHT</td>
<td>5</td>
<td>65.9</td>
<td>201.8</td>
<td>2092 2958</td>
</tr>
<tr>
<td>RFT</td>
<td>5</td>
<td>56.2</td>
<td>157.6</td>
<td>2127 2968</td>
</tr>
<tr>
<td>OID</td>
<td>6</td>
<td>50.5</td>
<td>117.6</td>
<td>2115 2808</td>
</tr>
<tr>
<td>OST</td>
<td>5</td>
<td>60.4</td>
<td>149.8</td>
<td>2159 2858</td>
</tr>
<tr>
<td>OHT</td>
<td>5</td>
<td>58.0</td>
<td>163.8</td>
<td>2197 2881</td>
</tr>
<tr>
<td>OFT</td>
<td>2</td>
<td>61.1</td>
<td>148.1</td>
<td>2218 2769</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ash Element as Oxide, wt %</th>
<th>No.</th>
<th>SEP</th>
<th>Magnitude of Max. Prediction Error</th>
<th>Range of Input Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>10</td>
<td>1.38</td>
<td>2.81</td>
<td>29.15 56.45</td>
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<tr>
<td>Al(_2)O(_3)</td>
<td>13</td>
<td>0.74</td>
<td>1.33</td>
<td>9.12 27.34</td>
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<tr>
<td>Fe(_2)O(_3)</td>
<td>8</td>
<td>1.79</td>
<td>3.19</td>
<td>4.33 30.17</td>
</tr>
<tr>
<td>CaO</td>
<td>3</td>
<td>1.73</td>
<td>6.88</td>
<td>1.07 30.11</td>
</tr>
</tbody>
</table>

/*Is*/
Figure 1. Comparison of FTIR and ASTM Results for Pyrite, wt % of LTA (Solid Line - Parity, Dotted Line - Least-Squares $y = 0.985 \times 0.098$)

Figure 2. Spectral Residual for the Best (Coal PO), Typical (Coal EH) and Worst (Coal SL) Least-Squares Fits. Spectra Shown are Original LTA (A, D, G), Least-Squares Composite (B, E, H), and Difference (Original Minus Composite C, F, I).

Figure 3. PCR Model Results for $\text{Al}_2\text{O}_3$, wt % of Oxidized Ash (Best Model of Ash Properties).

Figure 4. PCR Model Results for Ash Softening Temperature (Reducing), °F (Worst Model of Ash Properties).
CHEMICAL NATURE OF SPECIES ASSOCIATED WITH MOBILE PROTONS IN COALS; A STUDY BY FIELD IONIZATION MASS SPECTROMETRY

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INTRODUCTION

Proton n.m.r. investigations of coals swollen in deuterated pyridine showed that the free induction decay /FID/ consists of Gaussian and Lorentzian components related to two populations of protons which have widely different degrees of rotational mobility (1-5). The Gaussian component of FID has been unanimously ascribed to the macromolecular part of the coal matter that is supposed to have very limited rotational mobility. These publications as well as the ensuing debates (6-8) however, reflected the controversy regarding the nature of the Lorentzian /mobile/ protons in coals.

One view is that all Lorentzian protons can be attributed to molecules that are free to rotate in cages of the macromolecular network. Since the free molecules may be differentiated in their sizes and may have restricted freedom of rotation, their spin- spin relaxation times may be also differentiated and account for numerous populations of various mobilities within the group of Lorentzian protons.

The other view is that a significant part of the Lorentzian protons, especially those of lower mobility, may be also associated with fragments of the macromolecular network that can rotate due to a single C-C or C-O bond linking such fragment to the network.

The controversy cannot be easily clarified; there is no experimental technique available that could isolate all the free molecules and would leave intact the macromolecular network.

A more realistic approach is a separation of a mixture of free molecules and structural units linked to the network by single bonds, after these bonds have been cleaved by heat treatment of the coal. An insight into the composition of such mixture can provide information on the nature of species that are likely to be associated with the mobile protons. It seems that pyrolysis-field ionization mass spectrometry can be used in order to attain this goal.

Recently, an improved experimental setup for time-resolved in-source pyrolysis /py./ field ionization /f.i./ mass spectrometry /m.s./ has been described (9) and examples of its application to studying various biomaterials have been shown. There is a number of characteristic features of the py.-f.i.m.s. that are relevant to coal studies. Due to an increase of temperature of a sample in the direct introduction system of the mass spectrometer at heating rates around 1 °C per second and recording magnetic scans in 10 °C intervals, the volatilized species are not effected by a
higher temperature than is needed for their volatilization and detection. High vacuum and short residence time of the volatiles in the ion source of the spectrometer also reduce significantly secondary reactions between the species. The volatiles undergo soft ionization in the high electric field to produce molecular ions, with essentially no fragmentation ions. Hence, the mode of heating and ionization coupled with frequent scanning, can provide information about the composition of the material. When the py.-f.i.m.s. is applied to a coal, a mixture of free molecules as well as some parts of the macromolecular network is volatilized (10). Heating a coal to around 500 °C in the mass spectrometer should result in thermal decomposition of various single bonds that link structural units in the network (11). Although it is difficult to ascertain whether all free molecules and the structural units in question are volatilized in the mass spectrometer, this volatilized material certainly represents a high proportion of them.

The present paper shows such py.-f.i.m.s. data for a low rank bituminous coal. More specifically, the molecular weight distribution of volatilized material as well as elemental composition of its major components, are determined.

EXPERIMENTAL

The coal studied, 78 % C and 15.8 % O daf, is derived from Carboniferous deposits from the Ziemowit mine in Poland. Its petrographic composition is: vitrinite, 60; exinite, 12; and inertinite, 40.

Proton n.m.r measurements of Zeeman relaxation for the same coal showed that the fraction of mobile protons is 32 % of all protons. Assuming that the content of hydrogen in the mobile and immobile phases of the coal is approximately the same, the relaxation measurements indicate that the coal mobile phase content is app. 32 wt % of organic material.

Previously the py.-f.i.m.s. of coals and their pyridine extracts has already been described (10) using this novel technique. About 100 micrograms of ground coal sample was heated in the high vacuum of a combined e.i/f.i./f.d. ion source of a double-focusing mass spectrometer (Finnigan MAT 731, Bremen, FRG). The sample was heated at a constant rate of 24 °C/min from 50 to 500 °C. The volatilization of the coal was 30 % daf. This end-temperature had been selected in such way that the yield of volatilization of the coal in the mass spectrometer was comparable with the mobile phase content in the coal. The temperature also corresponds to a rapid decrease of volatilization that is shown in figure displaying total ion current. Forty spectra were recorded electrically in the whole temperature range. The f.i. signals of all the spectra were integrated, processed and plotted using the Finnigan Spectro-System 200 to give a summed spectrum. Five measurements of the sample were recorded and their averaged, summed spectrum was finally obtained which is reproducible and representative of the coal.

High mass resolution /h.r./ f.i. mass spectroscopy was carried
out using the same py. conditions as above. The photoplate (Q2, Ilford, England) was exposed to f.i. ions in the range m/z 60-500 for about 10 min. The resolution obtained was between 10,000 and 20,000 /50 % valley definition/ with an average mass accuracy of approximately 0.003 Dalton /3 mmu/. The photographic plate was evaluated with a Gaertner comparator. Mass measurements were calibrated using perfluorokerosene. The accurate mass determinations allow the calculation of the elemental composition of the f.i. ions.

RESULTS AND DISCUSSION

The volatilization of the coal pyrolysed in the mass spectrometer to 500 °C corresponds to 30 wt %daf which is in accord with the mobile phase content of the coal, 32 wt % org. mat. The molecular weights of the volatilized components were in the range of 80 to 800 Daltons. However, most intense f.i. signals were found in the much narrower range from 230 to 430 Daltons; abundances above this range quickly decreased to negligible values. The f.i. mass spectrum in question is not displayed here, since a similar one from another coal has been shown elsewhere (10).

High resolution f.i. data are shown in the Table. They are related to the major components of the volatilized material; the data for species for which intensities on the photoplate were below 5 % are not included. nor are the data for species above 300 Daltons that could not be accurately measured under the selected experimental conditions. Thus, the Table shows elemental composition of the species that account for app. 50 wt % of the volatilized material.

The species represent all homolog series of hydrocarbons from CnH2n to CnH2n-28; of compounds with one oxygen atom from CnH2n-2O to CnH2n-30O; and with two oxygen atoms from CnH2n-6O2 to CnH2n-26O2. These formulae relate to compounds that contain one, two /such as naphthalene and indene/ and three aromatic rings /such as anthracene, cyclopentaphenantherene and benzoacenaphthene/ as well as four aromatic rings /such as pyrene, chrysene/ and five aromatic rings as in benzopyrene. There are from 1 to 8 carbon atoms in the alkyl substituents on the aromatic rings. It is worthy of note that the alkyl substituents are not long. Even if one assumes all alkyl carbons form one alkyl substituent on a ring, a substituent cannot be longer than Cg for indenes, Cg foracenaphthenes, fluorenes and anthracenes and C6 for benzenes and naphthalenes. Essentially the same applies to alkyl oxygen compounds.

Under the same py.-f.i.m.s. experimental conditions, compounds with normal and branched alkyl chains up to C32 were easily detected in natural waxes (13). Thus, the present results indicate that long alkyl compounds are not major constituents of the coal and discussing the FID signals of coal in terms of its "polyethylene structures" (B.C. Gerstein in reference 8) is not correct for the coal studied and may be not correct for other coals.

In summarizing, the following statements can be made:
Py-f.i.m.s. of coal can provide information on chemical nature of species that most likely contain protons detected by n.m.r. experiments as mobile protons.

The results for a low rank bituminous coal show a high diversity of molecular weights for such compounds, from 80 to 800 Daltons.

The high resolution F.i. data, although limited to major components, also show diverse structures: the number of aromatic rings is from 1 to 5; the number of carbon atoms in alkyl substituents is in the range from 1 to 8.

This structural diversity must account for the wide range of rotational mobilities of the components of the mobile phase.

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EXPERIMENTAL OBSERVATIONS CONCERNING THE
TWO-COMPONENT CONCEPT OF COAL STRUCTURE

by
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Sutcliffe Speakman Carbons Ltd,
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Abstract
The hypothesis that coals can be considered to consist of two component groups has its origins in observations of coal behaviour as well as deriving from the analysis of coals and attempts to define their structure. The results of extensive studies of untreated, preheated and hydrogenated coals, using analytical and microscopic techniques, have allowed some insight into the association between the so-called mobile phase and macromolecular network, and have provided information upon differences in their chemical properties.

The yield of chloroform-soluble extract has been used to indicate the extent of the mobile phase. In untreated coals, only a portion of the mobile phase is readily removable. After mild preheating or mild hydrogenation, there are sharp increases in the yield of extract and accompanying changes in properties. Under these conditions, it is believed that weak binding between the mobile phase and network is disrupted. The solubilisation of the network requires much higher energy input and necessitates the consumption of hydrogen. The properties of the network components differ significantly from those of the mobile phase and both are coal rank-dependent.

Introduction
Much of the research pursued jointly by the authors and their associates has involved studies of the catalytic hydrogenation of coals in the absence of solvent. The aims have been to utilise this technique to try to elucidate the mechanisms of catalytic coal liquefaction and simultaneously to provide some insight into coal structure. The concept that, in broad terms, coals can be considered to consist of two distinct groups of constituents has been a particular focal point. The hypothesis is not new and has been advanced in a number of ways since the early part of this century. Its revival in recent years is largely attributable to the efforts of the late Peter Given to whom is also owed the now wide usage of the expressions 'mobile phase' and 'macromolecular network' (1,2).

To allow some clarification for a general readership, brief definitions of these terms will be attempted. The mobile phase comprises the smaller molecules in coals, some of which are extractable in solvents. The insoluble portion of coal is primarily a three-dimensional cross-linked macromolecular network or matrix. The mobile phase is attached to or held with the network by physical constraints and weak chemical bonds.
Peter Given was directly instrumental in providing the initiative and impetus which originated the authors' research. These efforts have extended since 1983. Previous findings were disseminated through several publications (3-7). In this paper, some of the earlier data have been collated with more recent (8) and hitherto unpublished results to provide an account of the relevance of these studies to the two-component concept.

Experimental

Coals covering a range of rank downwards from low-volatile bituminous were examined in solvent-free catalytic hydrogenation over the temperature range 300-400°C and for reaction times up to 60 min. The work discussed here specifically involved four coals which were obtained from the Penn State Coal Sample Bank. These were a subbituminous coal (PSOC-1403) and three hvAb bituminous coals, PSOC-1168, PSOC-1266 and PSOC-1510. Characteristics of the coals are summarised in Table 1. The reactors were of the tubing bomb type and the initial (cold) hydrogen pressure was 7 MPa. A sulphided Mo catalyst was introduced to the coal by impregnation from an aqueous solution of ammonium tetrathiomolybdate.

The gaseous products, chloroform-soluble extracts and chloroform-insoluble residues were characterised using a range of analytical techniques. A particular advantage of conducting the hydrogenation reactions in the absence of solvent is that microscopy can be used to observe directly the changes wrought in the whole reacted coals and in the extracted residues. Considerable emphasis was placed on this method of analysis using both visible light microscopy and quantitative fluorescence microphotometry. Detailed descriptions of the procedures and techniques have been given earlier (3-7).

Results and Discussion

Catalytic Hydrogenation

Detailed examination of the composition and distribution of the reaction products over a range of reaction conditions showed that the four coals exhibited certain common trends. Of particular note, there was in each case, a sharp distinction between the events which took place at low and high conversions. The division occurred at a chloroform-solubles yield of approximately 25% wt dmmf coal.

Low extract yields were obtained either by short reaction times at high temperatures or by more extended reaction at low temperatures. The designations of high and low temperature depend upon the individual coal and, more especially upon the coal rank. The evidence accrued in this research has shown that there exists a threshold temperature below which the potential for liquids formation is minimal and above which conversion can proceed at an appreciable rate.

It is supposed that this temperature is essentially determined by the density and nature of the crosslinks in the macromolecular network. This is consistent with evidence showing that the ease of conversion and the selectivity to lower molecular weight liquids increases with decreasing coal rank (8,9). For the subbituminous coal, the rate of liquids formation was negligible at 300°C and became appreciable at 350°C and higher. The bituminous coals began to
respond only at temperatures around 400°C. Similar observations have been made in experiments which compared the solvent-free hydrogenation of a lignite and a bituminous coal (10).

During the initial stages of conversion, as the liquid yield increased there were radical changes in the properties of the chloroform-soluble extracts. The H/C atomic ratio, aliphatic hydrogen content and oil to asphaltene (O/A) ratio each increased rapidly at first, passed through a maximum and decreased equally precipitately to a lower value, as illustrated in Figure 1. The curve shown for the O/A ratio is typical of the behaviour exhibited by the other coals.

A notable distinction was that the magnitudes of the changes were different for the subbituminous coal and the group of bituminous coals. Examples of the differences between the values for the parent coal extracts and the maxima are: H/C ratio 1.46 to 1.60 for the subbituminous coal, PSOC-1403, and 1.01 to 1.06 for the bituminous coal, PSOC-1266; O/A ratio 0.8 to 8.0 for PSOC-1403 and 0.25 to 1.5 for PSOC-1266.

At the maxima, 'H n.m.r. and elemental analyses showed that the greater proportion of the extract hydrogen was aliphatic: 10.5% for PSOC-1403 and 6.9% for PSOC-1266. In all cases over 90% of the total hydrogen content was aliphatic at this point. The high aliphatic hydrogen content was associated with the presence of polymethylene chains. The early release of paraffinic material, as n-alkanes and as long chain substituents to aromatic structures, under conditions of mild pyrolysis has been observed in other research (11-13). Over the initial period of conversion, it was also observed that only small quantities of light hydrocarbon gases were produced.

For the four coals, the maxima occurred between 5-10% wt extract yield and the subsequent decreases were arrested between 20-35% extract yield. No distinction could be made on the basis of coal rank although, admittedly, the number of coals is small.

The production of extract yields in excess of 20-35% wt marked the second stage of conversion. Over this period, the H/C atomic ratio and the total aliphatic hydrogen content remained approximately constant or decreased only gradually while the O/A ratio passed through a shallow minimum, Figure 1. The secondary gain in selectivity to oils at high conversions may represent the interconversion of asphaltenes to oils after extended reaction of the primary dissolution products. Other phenomena associated with the progress of the second stage were that the production of light hydrocarbon gases increased, the aromaticity of the extract progressively increased and oxygen functionalities were eliminated.

The consumption of gaseous hydrogen mirrored the changes described above, Figure 1. For the bituminous coals at 400°C, the initial rate of hydrogen uptake was very low. With further reaction, it accelerated, passed through a maximum, and then fell to a lower, more steady value. After about 60 minutes reaction, the total consumption was about 1.5% wt dmmf coal (about 2.0% wt for the subbituminous coal). At the point of transition from the slow initial rate to the accelerating rate, the liquid yields were between 5-15% wt dmmf coal. The acceleration in hydrogen uptake coincided with the end of the first phase of conversion. At this juncture, the total hydrogen consumed was 0.1-0.2% wt. The corresponding figure for the subbituminous coal was about 0.3% wt.
The existence of two stages of conversion has been separately demonstrated in studies by Mobil R & D Corporation where, in non-catalytic solvent liquefaction, two kinetic regimes were distinguished. Initial conversion was rapid with low attendant hydrogen consumption while subsequent conversion was slower and created a much greater demand for hydrogen (14). These findings were re-confirmed in later studies by the same group, when it was further shown that the products first formed were of higher H content and more aliphatic than those generated in the second regime. A subbituminous coal was found to consume more hydrogen than a bituminous coal at the same level of conversion (15).

The foregoing observations have direct implications to coal structure. In the present work, the production of liquids is facile below about 15% liquids yield and requires little hydrogen consumption. The processes most probably involve the release of species which are physically trapped or are weakly bonded to the insoluble matrix. At high conversions, the products are derived from the breakdown of the macromolecular network. This phase of conversion requires the cleavage and stabilisation of strong bonds, thereby creating an appreciable demand for hydrogen.

The products formed during the two stages are quite different in composition which can account for the rather dramatic swings observed in the extract properties with increasing conversion. The hydrogen-rich aliphatic products, which are first liberated, are responsible for the initial increases in the measured parameters. Later, as they become progressively diluted by more aromatic materials emanating from the network, the properties pass through a maximum and then decrease.

**Fluorescence Microscopy**

The phenomenon of vitrinite fluorescence has been described for 76 humic and vitrinitic materials with levels of organic maturation ranging from peat to low volatile bituminous coal (5,6). Figure 2a shows that fluorescence intensity decreases sharply through the series peat - peat/lignite transitional materials - lignite - subbituminous coal. The so-called primary fluorescence within this range is believed to be due to the presence of fluorophors derived from biopolymers, especially lignin. A second peak in fluorescence intensity (Fig. 2b) commences at about subbituminous rank, is reached in coals with a vitrinite maximum reflectance of about 0.9%, and is largely lost by medium volatile bituminous rank. This "secondary fluorescence" is attributed mainly to the presence of the mobile phase, a conclusion which is supported by a notable parallelism among the trends, in this rank range, of fluorescence intensity, chloroform-solubles yield and Gieseler maximum fluidity (5). The spectral distributions of the secondary fluorescence undergo a red shift due to the increasing conjugation of double bonds which accompanies coalification.

After chloroform extraction, coals still demonstrate low levels of residual fluorescence (Fig. 3), interpreted as being due to entrapped portions of the mobile phase. The figure also shows that mild thermal pretreatment (350°C for 3 min; N₂ atmosphere) considerably enhanced the intensity of fluorescence which subsequently was entirely removed by extended chloroform extraction (6). Apparently the heat treatment disrupts the bonding between network system and mobile phase, resulting in increased yield; with reduced energy transfer between the two phases, there is less possibility for intermolecular quenching, so that fluorescence intensity is enhanced.
Brown and Waters (16) showed that the yield of chloroform-soluble extract could be increased several-fold by coal pretreatment which involved rapid heating and cooling. The liberation of additional extract by this means is identical to the situation described above. The enhanced yields reported by Brown and Waters are of the same order as those corresponding to the initial conversion stage in the catalytic hydrogenation experiments. As this first stage incurred little or no net consumption of hydrogen external to the coal, it is believed that the effects of preheating and of low severity catalytic hydrogenation are equivalent. Brown and Waters concluded that the material derived by preheating was originally present as such in the coals and was not a product of pyrolysis. This is more or less the same definition of the mobile phase as it is understood in the present research.

Just as the untreated bituminous coals showed a parallelism among chloroform-solubles, vitrinite fluorescence intensity and Gieseler plasticity, the products of a single hvAb coal (PSOC-1510), hydrogenated for varying reaction times with a sulfided molybdenum catalyst, showed similar interrelations (Fig. 4). These results, together with the observation that chloroform-extracted coals lose their capability to become thermoplastic (17), are convincing evidence that the mobile phase is a necessary agent in promoting fluid behaviour.

Chloroform extraction of the whole products of dry hydrogenation (400°C; 60 min; 5% Mo; 7 MPa Hz) of PSOC-1266 produced a strongly fluorescent extract and non-fluorescent residue. After drying, the extract was seen under the microscope to contain two components with distinctive fluorescence characteristics (Fig. 5). Component 1 had a fluorescence spectrum very similar to that of the oil (hexane-soluble) fraction of the same hydrogenation products; component 2 had a spectrum like that of the corresponding asphaltene fraction, which, in addition to a higher peak wavelength, had a very much lower fluorescence intensity than the oil fraction. The observed differences in the fluorescence characteristics of the oil and asphaltene fractions are believed to be due to the more highly condensed materials which constitute the latter.

As reaction conditions became more severe, the fluorescence spectra of the hydrogenated vitrinite underwent a red shift (Fig. 6) from around 600 nm at 350°C to around 680 nm at 400°C. The trend is believed to be due to the production of a higher proportion of asphaltene material from the vitrinite network, as shown earlier by the reduction in O/A ratio with increasing conversion.

Synopsis

The liquefaction behaviour of the four coals investigated allows a general definition of the mobile phase as that material which is readily liberated by mild thermal treatment. The mobile phase components are richer in hydrogen and significantly more aliphatic than the structural units which comprise the network. The latter are connected by much stronger bonds, necessitating more severe reaction and higher hydrogen consumption to secure their release. The compositions of the mobile phase and network are also dependent upon coal rank.

Fluorescent light microscopy allowed a distinction between the extractable liquids, which fluoresce strongly, and the matrix, which does not. The disruption of weak bonding effected by thermal treatment, which increased the
extract yield, was paralleled by changes in fluorescence intensity. The fluorescence spectra of the extracts also reflect the compositional differences between the mobile phase and the solubilised coal network.

Based upon solubility in chloroform, the mobile phase is estimated to constitute 5-15% wt of the coal. Obviously, this amount will vary if other characterising solvents are used.

It is to be expected there will be a gradation in the manner in which the smaller molecules are associated with the network. This may involve both physical and chemical forces such as covalent bonds; dispersion forces; hydrogen bonding; and could involve physical entrapment. It is doubtful whether any single technique can distinguish between these different modes of attachment sufficiently clearly to establish a precise boundary. Different energies will be required to disrupt the different types of attachment. It may be significant that Brown and Waters (16) found that the increase in chloroform-soluble yield upon coal preheating was dependent upon the pretreatment temperature. A minor peak in the yield was observed at temperatures in the region of 300°C and a second major one at 400-450°C.

The particular experimental studies, which have been described here, have provided a basis for a practical definition of the boundary of the mobile phase in coals and some tentative clues to the nature of its association with the network. Inevitably, other research techniques will provide a different perspective.

Acknowledgement

The authors wish to acknowledge Peter Stansberry and Maite Terrer whose individual and collaborative research work provided the basis for this contribution.

References


Table 1. Coal Properties

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<td>hvAb</td>
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(a) reported as ASTM ash  
(b) by difference  
(c) by low-temperature ashing

682
Figure 1. RELATIONSHIP OF H₂ CONSUMPTION AND O/A RATIO FOR hvAb COAL, PSOC-1255 (solvent-free hydrogenation; 400°C; 1% wt. sulfided Ni; 7 MPa H₂)

Figure 2. PRIMARY AND SECONDARY VITRINITE FLUORESCENCE (Absolute Units)
(a) PRIMARY FLUORESCENCE IN U-V IRRADIATION
(b) SECONDARY FLUORESCENCE IN BLUE-LIGHT IRRADIATION

Figure 3. PEAK FLUORESCENCE INTENSITY OF RAW (▲) AND EXTRACTED VITRINITES (△) VERSUS YIELD OF CHLOROFORM-EXTRACTABLES. Also shown are data for thermally pretreated vitrinite before (○) and after (□) prolonged chloroform extraction (ref.6)
Figure 4. RELATIONS AMONG FLUORESCENCE INTENSITY, CHLOROFORM-SOLUBLES YIELD AND GIESLER PLASTICITY FOR HYDROGENATED COAL (PSOC-151; solvent-free; 400°C; 5-60 min; 1% wt sulfided Mo; 7 MPa H₂ cold)

Figure 5. COMPARISON OF FLUORESCENCE SPECTRA OF TWO COMPONENTS IN CHLOROFORM-SOLUBLES FRACTION WITH OIL AND ASPHALTENE FRACTIONS OF HYDROGENATED COAL (PSOC-1266; solvent-free; 400°C; 60 min; 5% wt sulfided Mo; 7 MPa H₂ cold)

Figure 6. FLUORESCENCE SPECTRA OF VITRINITE FOLLOWING HYDROGENATION AT 350 AND 400°C (PSOC-1266; solvent-free; 60 min; 5% wt sulfided Mo; 7 MPa H₂ cold)
A Study of the Proposed Two Phase Model for High-Volatile Bituminous Coals

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Introduction

It has been proposed that coal is composed of macromolecular networks and relatively small molecules occluded in macromolecular networks. This idea is known as a so-called two phase or host-guest model, which states that a mobile (molecular) phase or a "guest" of relatively low molecular weight such as a pentacyclic triterpane and various long chain alkyl aromatics is physically held inside an immobile (macromolecular) phase or a host of relatively high molecular weight. This is alternatively interpreted as a modified model in which some portions of the mobile phase are bonded to the immobile phase, however, it is thought that a substantial portion of the mobile phase is clathrated within the immobile phase.

Extraction were investigated in 1960 to early 1970; they were reestimated in late 1970 to early 1980 as components with mobile protons since the 1H NMR free-induction decay was applied for coal to distinguish between mobile protons and immobile protons. Many works have been recently reported to characterize the two phase model, and there seems to be consensus by them that only some portions of a mobile phase can be extracted using conventional extraction procedures because of restricted orifice sizes of immobile phases or networks. However, there is no direct evidence to prove the two phase model.

In this paper, the two phase model was studied by two sets of experiments. One used a combination of chemical class fractionations of coal extracts and mild pyrolyses of coals and extracts. Another used a n-butylamine treatment of coal followed by two different pyrolyses. The concentrations of n-alkanes, polycyclic aromatics (PAH), and pentacyclics, regarded as representative compounds in the mobile phase, were carefully determined. It is concluded that the two phase model is not applicable for high-volatile bituminous coal. It is also inferred that major constituents of coal are uniformly abundant in both extracts and residues.

Experimental Section

Five different rank coals were obtained from Exxon Research and Engineering Co. (Annandale, NJ). ACS reagent and HPLC grade solvents were used. Palladium on activated carbon (10%) was obtained from Alfa Products (Danvers, MA). Tetrahydrofuran (THF) was distilled before use, but other materials were used without purification.

Illinois No. 6 coal was treated as outlined in Figure 1. The coal (6g) was put into a 300 mL bomb (Parr Instrument Co., Moline, IL) in a removable Pyrex liner. After adding n-butylamine (25 mL), evacuating, and purging with N₂ five times, the bomb was heated to 350°C within 10 min with a Parr bomb heater, held at 350 ± 3°C for 4 h with agitation with a magnetic stirrer.

After treatment, the products were washed out with THF, filtered, and Soxhlet-extracted with THF. One part of the THF extract was hydrotreated.
following the Mudamburi and Given's procedure. A sample (2g) was heated with tetralin (5.6 mL) and H₂ (initial pressure 6.5 MPa) in a tubing bomb heated by immersion in a preheated fluidized bed sand bath for 30 min at 425°C. Another sample (2g) was pyrolyzed in cyclohexane (30 mL) and 3% aqueous H₂O₂ (3 mL) at 350°C for 30 min in a bomb. The sample (0.3g) after H₂O₂ treatment was further refluxed in decalin (50 mL) with Pd (10%) on activated carbon (300 mg) at 190°C for 24 h. These samples were put into Pyrex glass flasks under a dry N₂ atmosphere and were heated at 250 ± 1°C and about 660 mmHg pressure under N₂ flow in a Forma Scientific high-temperature vacuum oven 24 h as shown in Figure 2. Starting and pyrolyzed samples (2 - 3 g) were extracted with 200 mL of THF for 24 h in a Soxhlet apparatus under N₂ atmosphere. These extracts were fractioned into chemical classes by column adsorption chromatography on neutral alumina. The fractionation scheme is summarized in Figure 2. The aliphatic and neutral aromatic fractions were analyzed in this study.

Hewlett-Packard Model 5840A gas chromatograph (GC) equipped with a flame ionization detector was used. Sample injection was made in the splitless mode, and helium carrier gas was set at a linear velocity of 50-60 cm s⁻¹. The fused silica capillary tubing (30 m x 0.25 mm i.d.) coated with SE-54 (film thickness of 0.25 μm) was obtained from SUPELCO, INC. (Bellefonte, PA). Compounds were identified by comparison of sample component retention data with those of pure standards and by gas chromatography/mass spectrometry (GC/MS). Mass spectral data were collected with a Hewlett-Packard 5970 mass spectrometer system operated in the electron-impact mode at 70 eV with the ion source and analyzer temperature held at 250 and 280°C, respectively, with the scan speed set at 300 amu s⁻¹.

### Results and Discussion

Given's et al. reported that the yield of n-alkanes and n-alkyl aromatics released from coals by liquefaction in tetralin at 400-425°C was 6-10 times greater than the yield obtained by Soxhlet extraction. They found it difficult to conceive of such homologous series being released from the macromolecular network by thermal reactions, and inferred that the compounds were clathrated inside the network. It is, however, impossible to distinguish between the disruption of chemical bonds and physical bonds using their data. Since most of the organic matter of high-volatile bituminous coals could be extracted with THF after mildly heating in n-butylamine, n-alkanes and PAH were analyzed for the THF extracts from an original and n-butylamine heated coals to investigate physically trapped low-molecular-weight compounds. The THF extract from the n-butylamine heated coal was pyrolyzed using the Given's procedure as well as another different method to differentiate between breaking covalent bond and physical forces (Figure 1). Although the detailed solvation mechanism in n-butylamine is not clear, the differences of abundances of such compounds between Sample II and Sample III or IV are unequivocally due to degradation of chemical bonds. (See Figure 1)

The yield of Sample II from the Illinois No. 6 coal was approximately 85 wt %, which was normalized for the extract and the non-extract because of 18 wt % of the weight gain after heating in n-butylamine. Relative abundances of n-alkanes in the Samples were semi-quantitatively analyzed by GC. The results are shown in Table I relative to n-C₂₀H₄₂ in Sample I. It is obvious that the yields of these compounds in Samples III and IV are greater than 10 times of those in Samples I and II, while the yields of these compounds in Samples I

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and I1 are almost comparable. From this result, it can be concluded that the increased compounds in Samples III and IV were mostly derived from the thermal pyrolysis of macromolecules, and were not released from clathrated compounds inside the network or immobile phase.

Figure 3 shows the gas chromatograms of the aliphatic fractions of Samples I, II, and IV. It is obvious that n-alkanes with carbon numbers 17 to 22 were relatively increased from Samples II to IV by the pyrolysis. Pentacyclic triterpanes are presumably thermally labile compared with p-alkanes, and their abundances decreased in the order of Samples I, II, and IV as expected. The relative abundances of the major PAH in Samples I - V are also shown in Table I relative to phenanthrene in Sample I. These compounds in Samples III - V were noticeably increased by thermal reactions similar to the n-alkanes. They are apparently important partial constituents of coal macromolecules, or derived from macromolecules during pyrolysis.

It can be interpreted that the great increase of p-alkanes in the product obtained by Given et al. was due to the degradation of coal macromolecules, because more than 10 times of p-alkanes originally present in Illinois No. 6 coal extracts were formed from p-butylamine extracts under their reaction conditions. It is proposed that p-alkyl groups are one of important constituents of Illinois No. 6 coal macromolecules, and most of the p-alkanes in coal-derived products were formed from high molecular weight compounds.

The Illinois No. 6 THF extract and a dried mixture of fractions A-3 and A-4 were heated at 250 °C for 24 h and fractionated into chemical classes as shown in Figure 2. Since high-molecular-weight aromatic Compounds strongly adsorb on neutral alumina, they are not eluted by benzene but are found in the A-3 and A-4 fractions.26 Figure 4 shows gas chromatograms of the A-2 (aromatics) fractions of these heat-treated samples as well as the A-2 fraction of the original coal extract. Significant amounts of material were found in fractions A-1 and A-2 after heating the extract fractions A-3 and A-4 to 250 °C for 24 h. Simply refractionation a mixture of A-3 and A-4 gave very little material in the A-1 and A-2 fractions, so it is clear that the origin of the new compounds is pyrolysis. Furthermore, many new peaks are found in the chromatograms of these fractions. Clearly new compounds are present. Their-alkanes from these heat-treated samples as well as the A-2 fraction. Significant amounts of material were found in fractions A-1 and A-2 after heating the extract fractions A-3 and A-4 to 250 °C for 24 h. Simply refractionation a mixture of A-3 and A-4 gave very little material in the A-1 and A-2 fractions, so it is clear that the origin of the new compounds is pyrolysis. Furthermore, many new peaks are found in the chromatograms of these fractions. Clearly new compounds are present. Their analysis reactions occurred by thermal pyrolysis of the original coal extract at 250 °C. Among the new compounds are a number of low-molecular-weight aromatic compounds such as alkylbenzenes, alkylnaphthalenes, phenanthrene, and alkylhydroaromatic triterpanes, presumably formed by pyrolysis of the high-molecular-weight fractions. Both results, obtained by different experimental procedures, are clearly consistent.

There were two purposes for the reaction leading to Sample V. One was to confirm the identification of the hydroaromatics, because it is known most of the hydroaromatics are dehydrogenated by Pd on activated carbon at the low temperature used in this study. The second was to investigate the effect of aromatization by dehydrogenation during coal liquefaction.

Hydroaromatics such as hydroanthracenes, hydrophenanthrenes, and hydropyrenes were abundant in Sample IV compared to Sample III, while 4- and 5- ring PAH such as chrysene and benzopyrenes were abundant in Sample III (Table I). It is thought that the major reaction producing Sample IV from Sample II is a mild radical cracking while the major reaction involved in forming IV from Sample II is hydrocracking including thermal aromatizations at high temperature. Hydroaromatics, therefore, seem to be one of important constituents of coal macromolecules. Although aryl groups such as biphenyls...
and phenylnapththalenes are abundant in Samples III and IV. Carbon linked aromatics were not found in these samples at a significant level. The abundances of the aliphatics and aromatics in Sample V are quite similar to other coal liquids such as the Solvent-Refined Coal II heavy distillate (SRC II HD), although the feedstock was a different coal.

From above results, we can infer as the follows: coal components are quite uniform despite extracts or non-extracts. Most n-alkanes and PAH are not physically trapped inside networks. They are both free molecules and partial constituents of macromolecules or derived from macromolecules during pyrolysis, and can be thought as "preferred" constituents. Most the neutral free low-molecular-weight compounds can be extracted under conventional conditions, such as a Soxhlet extraction.

Since the two phase model does not appear to be appropriate for Illinois No. 6 coal, the coal should be considered as a mono phase. Coal molecules contain "preferred" components such as n-alkanes and PAH studied in this paper. The preferred components are estimated for Illinois No. 6 coal. It also seems that aromatics linked with a couple of carbons are not so substantial in Illinois No. 6 coal as above "preferred" structures.

The mono phase model and its "preferred" structures contained in the Illinois No. 6 coal are essentially different from the two phase model. The "preferred" molecules are partial constituents of coal macromolecules regardless of molecular weight, and some exist as free molecules of low-molecular-weight.

Acknowledgments

I thank M. L. Gorbaty, G. M. Kramer, and J. W. Larsen for their encouragements. Technical supports by D. J. McHuch and J. E. Bond are also acknowledged.

References

(4) Given, P. H.; Marzec, A. Fuel, 1988, 67, 242-244.
(17) Kamienski, B.; Pruski, M.; Gerstein, B. C.; Given, P. H. Energy & Fuels
Table I. Approximate Relative Abundances of Selected Compounds in Each Sample

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<th>Compound</th>
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<th>Sampleb</th>
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Relative abundances are shown as n-C20H42-l for aliphatics and phenanthrene-1 for aromatics.

a <0.01

\[1987, 1, 45-50.\]


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<sup>a</sup>Numbers in parentheses denote relative abundances of mass spectra.
Figure 1. Solvent treatment and reaction scheme of Illinois No. 6 coal.

Figure 2. Fractionation and pyrolysis scheme. Key: HMW = high-molecular-weight compounds.
INTRODUCTION

In recent years few topics have generated a more spirited discussion among coal scientists than the issue of the putative binary (mobile + network) phase nature of coals [1]. Initially based on NMR observations [2], the concept of a "mobile phase" in coal soon came to encompass a broad range of more or less readily extractable and/or distillable lower molecular weight (MW) components, variously referred to as "guest molecules" [3], "clathrates" [1,4] or simply, and perhaps most succinctly, "bitumen" [5].

None of these terms appears to be completely satisfactory. The concept of "mobility" in NMR spectroscopy is quite different from that in the field of separation science, where mobility generally requires a measurable degree of solubility and/or distillability in liquid or gaseous media, respectively. For example, polymethylene-like moieties, such as found in some coal components [6], are highly "mobile" in NMR terms [1], without necessarily being extractable by solvents or distillable by nondestructive heating.

None of these terms appears to be completely satisfactory. The concept of "mobility" in NMR spectroscopy is quite different from that in the field of separation science, where mobility generally requires a measurable degree of solubility and/or distillability in liquid or gaseous media, respectively. For example, polymethylene-like moieties, such as found in some coal components [6], are highly "mobile" in NMR terms [1], without necessarily being extractable by solvents or distillable by nondestructive heating.

The term "guest molecules", originally introduced to indicate specifically labeled marker molecules used in NMR studies of coal [7], is equally unsatisfactory for mobile phase components indigenous to the coal itself. Also, it appears to be insufficient evidence for the presence of sizeable quantities of true "clathrates" to rule out other possibilities, e.g., strong noncovalent bonding rather than physical entrapment.

Finally, completely equating the "mobile phase" with solvent (e.g. pyridine) extractable "bitumen" in coal ignores the potential presence of colloidal particulate matter in the pyridine extracts as well as possible solvent-induced scission of weak chemical bonds. Furthermore, the solvent-extractable fraction may well include macromolecular components, such as resinites.

Mass spectrometric observations have thus far played a rather limited role in the "mobile phase" discussions [1] but are starting to shed some light on the key question: is there conclusive evidence for the presence of a chemically and/or physically distinct "mobile phase", as opposed to a continuum of possible molecular sizes and structures?

In the context of the present discussion the term "mobile phase" will be used to describe those components which can be thermally extracted ("distilled", "desorbed") under vacuum at temperatures below the thermal degradation range of the coal. The residue, designated as the nonmobile ("network") phase, is
thermally degraded in the pyrolysis temperature range. Of course, the onset of pyrolysis may vary considerably, depending on heating rate, rank and coal type [8].

EXPERIMENTAL

Two samples of -100 mesh ANL-PCS (Argonne National Laboratory-Premium Coal Sample) coal, a Pittsburgh #8 seam (hvAb) and a Beulah Zap seam (lignite) sample, were analyzed by vacuum pyrolysis field ionization mass spectrometry (Py-FIMS) and Curie-point pyrolysis low voltage electron ionization mass spectrometry (Py-EIMS) in the time-resolved (TR) mode. In addition, a sample of fresh -60 mesh Hiawatha seam (hvBb) coal, obtained from an Emery County (Utah) mine was analyzed by TR Py-EIMS. Conventional characterization data on ANL-PCS coals can be found elsewhere [9].

For temperature-programmed pyrolysis in combination with TR-FIMS, about 100 ug samples were transferred into a quartz crucible and introduced into the high vacuum (10^{-3} Pa) of the ion source (200 C). The instrumental setup using a Finnigan MAT 731 double-focussing mass spectrometer, a combined EI/FI/FD/FAB ion source and a AMD Intectra direct introduction system has been previously described in detail [10]. The samples were heated linearly from 50 C to 750 C at a rate of 100 C/min. In general, 34 FI mass spectra were recorded in the m/z 50-900 mass range.

The Py-EIMS experiment was performed using an Extranuclear 5000-2 Curie-point Py-MS system. The coal sample was hand ground into a fine, uniform suspension in Spectrograde methanol (5 mg of sample per ml of methanol). A single 5 μl drop of the suspensions was coated on the ferromagnetic filament (Curie-point temperature of 610 C) and air-dried under continuous rotation for approximately 1 min, resulting in 25 μg of dry sample on the filament. The filament was inserted into a borosilicate glass reaction tube and introduced into the vacuum system of the mass spectrometer. Directly in front of the open, cross beam type electron ionization chamber the ferromagnetic wire was inductively heated for 0.4 s at a rate of approximately 1500 K/s to an equilibrium temperature of 610 C (as determined by the Curie-point temperature of the wire). The pyrolysis inlet was preheated at 200 C to reduce the condensation losses. Other MS conditions were as follows: electron impact energy 12 eV, mass range scanned 50-200 amu, number of scans 41, total scan time 15 s.

RESULTS AND DISCUSSION

Is there a chemically and/or physically distinct "mobile phase" in coal as opposed to a continuum of molecular sizes and structures? The temperature-resolved total ion intensity (TII) profile of a Pittsburgh #8 coal in Figure 1 obtained by temperature programmed Py-FIMS shows the presence of a low temperature "hump" which appears to explain 25-30% of the total integrated FI signal intensity in the mass range m/z 50-900. Previously, Chakravarty et al. [11] reported a similar profile for Pittsburgh #8 coal obtained by Curie-point pyrolysis in combination with time-resolved low voltage EIMS and were able to demonstrate that the low temperature hump consisted primarily of homologous series of alkylsubstituted aromatic (e.g., benzenes, naphthalenes, phenanthrenes) and hydroaromatic (e.g., tetralins) compounds. These compounds were interpreted to represent the thermally extractable ("vacuum distillable") fraction of the well known "bitumen" component of most high volatile bituminous coals.
More recently, Yun et al. [12] confirmed the presence of this low temperature hump in vacuum thermogravimetry (TG)/MS studies of ANL PCS coals using low voltage EIMS. An important aspect of the latter study was that the mass spectra obtained for the thermally extractable components as well as for the main pyrolysis event were found to be virtually indistinguishable from those observed by Chakravarty et al. using Curie-point Py-EIMS, notwithstanding a 5 orders of magnitude lower heating rate (3.3 x 10^{-2} C/s vs. 1.5 x 10^3 C/s) and 3 orders of magnitude larger sample (50 mg vs. 25 ug).

Furthermore, with proper preheating of the transfer zone between pyrolysis and ionization regions, the low voltage E1 mass spectra of Pittsburgh #8 coal were shown to be highly similar to the corresponding FI mass spectra in the m/z 50-300 mass range when allowing for known differences in ion transmissivity between the different types of mass spectrometers used [13]. In other words, time-resolved TII profiles similar to those shown in Figure 1 as well as to the corresponding mass spectra in Figure 2a have been observed (up till m/z 300) by means of 3 separate Py-MS methods, together covering a broad range of different pyrolysis, ionization and mass spectrometric detection techniques.

The advantages of the FIMS data shown here are that little or no fragmentation of molecular ions occurs during the ionization process and that FI response factors for aromatic and hydroaromatic compounds tend to show relatively little variation [14]. In combination with the large mass range and nearly constant ion transmissivity of the magnetic sector instrument used, the FI ion profiles and FI spectra shown in Figures 1 and 2, respectively, are suited for making reliable semiquantitative estimates with regard to relative the yield and molecular weight distribution of coal tar fractions consisting primarily of aromatic and hydroaromatic or alicyclic compounds. Unfortunately, FI response factors for aliphatic compounds show a great deal more variation [15]. Consequently, for the purpose of this discussion no attempt will be made to quantitate the contributions or molecular weight distributions of aliphatic components in spite of their well recognized role in coal pyrolysis processes.

Comparison of the low temperature component ("mobile phase") and high temperature component ("bulk pyrolyzate") spectra in Figures 2b and 2c, respectively, reveals roughly similar average molecular weights (M_n 350) but rather different MW distributions. Moreover, there are pronounced differences in relative FI signal intensities, especially in the mass range up to m/z 400.

Figure 3 shows the relationships between the temperatures and molecular weight distributions for 6 successive regions of the TII profile in Figure 1. Interestingly, regions a, b and c, primarily representing the low temperature components, show relatively narrow MW distributions around M_n values which markedly increase with temperature. This is consistent with the proposed interpretation of the low temperature "hump" as a vacuum desorption and distillation process rather than as a pyrolytic process. By contrast, regions d, e and f, representing the major TII maximum in Figure 1, exhibit much broader MW distributions characterized by a gradually decreasing average molecular weight of the pyrolyzate. This would seem to be consistent with the proposed interpretation of the major TII peak as the "bulk pyrolysis" event [11].

The transition between c and d is rather abrupt, suggesting that we may indeed be witnessing contributions from two more or less discrete populations of molecules with regard to molecular size distributions. However, in view of the extremely complex interplay between intramolecular and intermolecular, as well
as intraparticle and extraparticle, parameters in the experiments described here, the possible presence of a continuum of molecular sizes can certainly not be ruled out at this point.

More informative, perhaps, are the marked differences in relative FI signal intensities between the mass spectra shown in Figures 2b and 2c. In agreement with the previously mentioned results reported by Chakravarty et al. [11] and Yun et al. [12], the mass spectrum of the low temperature component (Figure 2b) appears to be dominated by homologous series of aromatic and hydroaromatic compounds. Chemical identification of many of the compounds up to MW 350 has been accomplished by high resolution GC/MS [16,17], although precise identification of the many possible isomeric structures involved will have to await the availability of suitable reference compounds.

The spectrum of the bulk pyrolysis event in Figure 2c appears to be dominated by hydroxy aromatic compounds, e.g., alkylsubstituted phenols and naphthols. Positive identification of these compounds is much less straightforward, although a surprisingly high degree of correspondence can be found with Py-GC/MS data on Pittsburgh #8 coal [18]. Moreover, Chakravarty et al. have demonstrated that the main pyrolysis event can be deconvoluted into at least three overlapping events involving vitrinitic moieties in addition to alginite/cutinite-like and sporinite-like components [11].

In Curie-point Py-MS studies of maceral concentrates [19], vitrinitic moieties were shown to be the main source of the hydroxy aromatic components. Consequently, the hydroxy aromatic signals observed in Figure 2c appear to be primarily derived from vitrinite-like components by means of pyrolytic processes. Presumably, therefore, the "nonmobile phase", rather than the "mobile phase", is the main source of the phenols observed in TG/MS and Py-MS studies of Pittsburgh #8 coal. Further support for this conjecture comes from the observation that phenolic products are also observed in Py-MS analysis of pyridine extracts of Pittsburgh #8 coal known to contain colloidal matter whereas the corresponding tetrahydrofuran extracts, free of colloidal material, produced no phenols [18].

In low rank coals, such as lignites, vitrinitic components have been shown to produce abundant (alkyl) dihydroxy benzene and methoxy hydroxy benzene compounds of a structural type which can be traced back to fossil lignin moieties [20]. In agreement with these earlier studies, the high temperature component spectrum of a Beulah Zap lignite (Figure 4c) exhibits dominant (alkyl) dihydroxy benzene signals at m/z 110, 124, and 138. The low abundance of FI signals above m/z 200 can be attributed to the more highly crosslinked nature of the macromolecular network phase in lignites.

As shown in Figure 4b, the low temperature fraction of Beulah Zap lignite reveals a completely different type of mass spectrum. From previous studies on soil organic matter by Hempfling et al. [21], the FIMS signals in Figure 4b are known to represent various plant-derived compounds such as n-fatty acids or monomeric esters (m/z 368, 396, 424, 452, 480) and aromatic diesters (m/z 544). Apparently, we are dealing with thermally extractable "biomarker" compounds which have not yet been linked into the macromolecular network phase of the lignite.

The above observations point to the importance of rank and depositional environment in defining the molecular characteristics of the "mobile phase" as
well as the "network phase" of coals. To complicate matters further, post-depositional factors, such as "weathering" during storage or transportation, also strongly affect the composition of both phases, as reported by Jakab et al. [22]. Figures 5 and 6 illustrate the effects of mild oxidation of a Hiawatha hvb coal for 100 hours at 100°C under controlled laboratory conditions, as measured by time-resolved Curie-point Py-MS. Both the low temperature hump as well as the bulk pyrolysis event are markedly reduced. Moreover, the composition and nature of the low temperature components have undergone a dramatic change (Figure 5b). The alkyl substituted naphthalenes and tetrains dominating the spectrum of fresh coal (Figure 5a) are nearly completely gone. Instead, we now find low MW, oxygen-containing mass signals apparently representing aliphatic carboxylic and carbonylic functionalities, e.g., liberated by low temperature pyrolysis of weak oxygen bonds [22]. These observations would seem to indicate that it is pointless to study "mobile phase"/"network phase" phenomena in coal samples of uncertain weathering status.

CONCLUSIONS

Temperature-programmed vacuum pyrolysis in combination with time-resolved soft ionization mass spectrometry allows principally to distinguish between two devolatilization steps of coal which are related to the "mobile" and "non-mobile" phase, respectively. The mass spectrometric detection of almost exclusively molecular ions of the thermally extracted or degraded coal products enables to study the change of molecular weight distribution as a function of devolatilization temperature. Moreover, major coal components can be identified which are released at distinct temperature intervals.

When limiting our analysis and discussion of mobile phase components to the thermally extractable fraction, we may conclude that the yields and compositions of these products (estimated to constitute 5-15% of dmnf coal weight) are strongly dependent on rank, coal type and weathering status. In coals of hvb and higher rank the nature of the thermally extractable bitumen fraction is consistent with that of a natural pyrolyzate formed by catagenetic processes during the "oil formation window" stage of maturation with subsequent loss of the more reactive oxygen containing moieties. Not surprisingly, in low rank coals various types of relatively little altered "biomarkers" molecules appear to be important constituents.

Furthermore, artificial "weathering" of coal under carefully controlled conditions in the laboratory, reveals a rapid loss of thermally extractable mobile phase components (possibly by "grafting" to the network phase [23]) accompanied by a decrease in total pyrolysis yields. This points out that in future discussions of "mobile phase" phenomena only results obtained on coals of known weathering status, e.g., ANL-PCS coals, should be used.

With regard to the central question whether there exists a chemically and/or physically distinct "mobile phase" in coals, mass spectrometric data on ANL-PCS coals (only 2 of 8 are presented here) strongly support the presence of a thermally extractable, bitumen-like fraction which is chemically distinct from the remaining coal components.

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Figure 1. Thermogram of a Pittsburgh #8 coal sample showing a distinct low temperature release of mobile phase components. Crosshatched intervals a-f correspond to molecular weight profiles of FI ions in Figs. 3a-f, respectively.

Figure 2. Comparison of Pittsburgh #8 (hvb) coal Py-FI mass spectra recorded over different temperature intervals. Note marked differences between low temperature components in (b), thought to represent primarily vacuum distillable "mobile phase" constituents, and high temperature components in (c), thought to represent mainly pyrolysis products derived from the macromolecular "network phase".
Figure 3. Molecular weight distributions of pyrolyzates in six successive temperature intervals during Py-FIMS analysis of Pittsburgh #8 coal. Each interval corresponds to a cross-hatched region in Figure 1. The FI signal intensities were added in arbitrarily chosen mass classes of 50 daltons.

Figure 4. As Figure 2 but representing Beulah Zap seam lignite. Note biomarker pattern of vacuum distillable low temperature component in (b). Further note marked difference with Pittsburgh #8 in Figure 2.
Figure 5. Time-resolved TII profiles of a Hiawatha seam (hvBB) coal obtained by Curie-point pyrolysis in combination with low voltage EIMS. Note effect of artificial "weathering" compare with Figure 6.

Figure 6. Comparison between low temperature component spectra obtained by low voltage EIMS. Note pronounced effect of mild artificial "weathering". Compare with Fig. 5.
MOLECULAR STRUCTURE AND CONFORMATIONAL STABILITY OF COALS

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ABSTRACT

Factors which influence the molecular conformation and stability of the organic fractions of coals are discussed. Data for an extensive suite of Australian coals from experiments using nuclear magnetic resonance techniques to measure the effects of heating and exposure to pyridine on the stability of coal molecular structures are presented. Two types of fusible material are identified and how these materials and their fusibility vary with coal rank are evaluated. Also the rank and maceral dependence of the destabilizing effects of pyridine are catalogued.

Key Words: Coal fusibility, NMR, macerals, molecular structure.

INTRODUCTION

The Molecular Properties of Coals

Dry coals are essentially organic solids at ambient temperature and, except for a degree of molecular mobility associated with aliphatic structures apparent from nuclear magnetic resonance measurements (1), they can be considered to be rigid molecular lattices. Although the molecular structures of organic substances profoundly affect their solid state properties, the molecular structure of coals has been little studied compared to their chemical composition and functionality. Studies of coal structure at any level are difficult because of the complex heterogeneity of any particular coal and the great variability of coal types that occur.

Broadly speaking three main concepts are used to model the molecular structure of coals:

1) Coals as macromolecular three-dimensional crosslinked viscoelastic glassy solids (2,3).
2) Coals as macromolecular/molecular two-phase systems - the host/guest or 'rigid' and 'mobile' phase model (4-6).
3) Coals as paracrystalline substances depicted as having amorphous and ordered micellar regions (7).

The major limitation to the usefulness of each of these concepts (and, no doubt, the necessity for all three) stems from the great variability of coal types. Also, these concepts have mostly been applied only to the vitrinite macerals.

Conformational stability and the molecular structure of organic solids are determined both by the nature of the molecular network (how discrete molecular units are connected by covalent crosslinks) and by the nature and distribution of the various non-covalent interactions amongst these units. The non-covalent interactions include localized (e.g. hydrogen bonds) and non-localized electrostatic interactions and the short-range non-polar interactions between molecular units due to the ubiquitous and weak van der Waals induction and London dispersion forces (8).

Thus in the case of the aromatic-rich (i.e. vitrinite and inertinite) macerals of coals, if the molecular units are considered to be condensed aromatic and hydroaromatic ring structures, the molecular conformation and stability of the
Macerals are determined by the density of covalent crosslinks, the degree of polar functionality and the size and geometry of the condensed ring units.

The aliphatic-rich liptinite macerals are comprised of a variety of structures including long-chain alkanes, polymerized alicyclic structures and hydroaromatic units (9). Their conformation is determined largely by covalent crosslinks and probably only to a minor extent by polar interactions.

One means of investigating molecular structures is to determine the extent to which a solid can be destabilized by heat prior to its pyrolytic decomposition.

Significant molecular mobility activated in brown coals at temperatures between 300 and 600 K has been related to the fusion of the extractable, aliphatic-rich fraction of the coals (10). Thermal destabilization of the molecular lattice of aromatic-rich macerals in bituminous coals at temperatures above ~600 K is associated with their characteristic thermoplasticity (11). The relationship between the extent of this fusion and the molecular properties of the vitrinite and inertinite macerals, however, is not well understood.

The interaction between solvents such as pyridine and coal can also be interpreted in terms of the structural features discussed above. How small nucleophilic molecules disrupt inter- and intra-molecular non-covalent interactions thereby 'relaxing' the structural matrix and allowing further solvent penetration has been extensively discussed by Peppas (12), Larsen (2,13) and Marzec (14,15) and their colleagues. Indeed the extent to which exposure to a solvent such as pyridine destabilizes a material's molecular structure is a measure of the extent to which the stability of the material depends on non-covalent and in particular polar interactions. Solvent destabilization of the molecular structure of organic materials can be quantified by simple NMR measurements at ambient temperatures. Such measurements have shown that up to ~60% of a coal's molecular structure can be destabilized by pyridine and, by the same token, that at least ~40% is impervious to pyridine (15-17).

Recently Qinga and Larsen (18) have considered the role of non-polar interactions in coals. In particular, they pointed out the likely importance of London dispersion forces between planar aromatic units and that the effect of these short-range interactions on the stability of a lattice would increase with increasing size of the molecular units. Thus the greater concentration and growth in average size of those units with increasing rank for bituminous coals lead to enhancement of the role of the London dispersion interaction in the stabilization of the molecular lattice of these coals. This process no doubt leads to the formation of the ordered graphite-like structures detectable by X-ray diffraction (e.g. ref. 7) and apparently not disrupted by exposure of the coals to pyridine and their resultant swelling (19). Also the microscopic conformal and reversible nature of the swelling of coals by pyridine established by Brenner (2) points to these ordered structures existing in microdomains of dimension less than ~10^{-8} m.

Strong evidence of the dominant influence of molecular structure on the properties of coals is implicit in the several data sets which show an extremum in the measured property when plotted against carbon rank. Examples are the extrema which occur in the solid state properties of mass density (20) and proton spin-lattice relaxation rate (21) as well as in solvent swelling and extractability (2).

Nuclear Magnetic Resonance Techniques

Proton nuclear magnetic resonance (1H NMR) measurements can distinguish hydrogen in rigid molecular structures of coals, i.e. structures that do not undergo appreciable reorientation and/or translation during time intervals <10^{-5} s, from hydrogen in mobile structures which possess more rapid molecular motions characteristic of fused or rubbery materials. The data provided by these measurements are presented in this paper in terms of a parameter $M_2T$ that measures...
the extent and degree of molecular mobility. $M_{2T}$ is an empirical second moment of the frequency spectrum of the NMR signal (22), truncated here at 16 kHz, and is inversely related to the average molecular mobility of the specimen. Thus the relative decrease in $M_{2T}$ is a sensitive measure of the extent and degree of mobility acquired by rigid molecular structures as a result of their destabilization by thermal or solvent treatment.

The technique of $^1$H NMR thermal analysis yields data in the form of $M_{2T}$ pyrograms (typical examples are shown in Figures 1 and 2). The fusibility of a coal can be ranked by the minimum value of $M_{2T}$ ($M_{2T}(\text{min})$) attained during the experiment.

Because the extensive property of a specimen measured by $^1$H NMR is the hydrogen content, in the data analyses described below maceral contents which are determined on a volume basis (denoted by vol%) have been converted to a wt% hydrogen basis (denoted by H-wt%) by the method of Lynch et al. (23). In practice, the changes produced in the maceral content values are small except for the coals richest in liptinite.

**EXPERIMENTAL**

Data have been obtained for an extensive suite of well characterized Australian coals by $^1$H NMR experiments which probe separately the effects of heat and the effects of exposure to the nucleophilic solvent pyridine on the molecular stability of the coals.

The coals and coal fractions which have been examined by $^1$H NMR thermal analysis are subdivided into two sets as follows:

a) 95 Australian bituminous coals (both whole coals and maceral concentrates including 10 pairs of vitrinite and inertinite concentrates obtained by density separation) with carbon contents of 80 - 89% (daf) and hydrogen contents between 4.1 and 6% (daf);

b) 25 sub-bituminous and brown coals with carbon contents of less than 80% (daf).

The vitrinite and inertinite (predominantly semifusinite and inertodetrinite) contents of these coals are in the ranges 10 - 98 and 5 - 80 vol% (mmf) respectively. The liptinite content never exceeds 22 vol% and is $\leq$10 vol% in most coals.

Pyridine swelling experiments involved a suite of 46 bituminous whole coals and maceral concentrates selected from set (a) above.

All coals were ground to $\leq$500 µm and acid-washed to remove HCl-soluble iron (24). The resulting specimens were stored at 255 K under nitrogen until they were dried overnight under nitrogen at 378 K immediately prior to thermal analysis or addition of pyridine.

The thermal analysis experiments involved the collection of $^1$H NMR data while coal samples were being heated at 4 K/min to 875 K under non-oxidizing conditions.

In the solvent swelling study each coal was soaked in excess deuterated pyridine in a sealed glass ampoule for approximately two months before NMR measurements were made at room temperature.

**DATA ANALYSES AND RESULTS**

**Thermal Analysis Data**

In Figures 1 and 2 the $M_{2T}$ pyrograms for seven representative coal specimens are plotted. Analytical data for these materials are listed in Table 1.
The M_2T pyrogram of a typical brown coal (a) reveals the significant thermally activated molecular mobility which occurs on heating from room temperature to ~ 600 K. This has been shown to be the result of fusion of the extractable component of these coals (10). The reduction in molecular mobility (increase in M_2T) above 600 K results mostly from volatile loss of this 'guest' material. The M_2T pyrogram of the extracted residue of a brown coal (b) which constitutes usually >80% of the total coal exhibits only a low level of thermally activated molecular mobility. The shallow minimum which does occur in this pyrogram is probably due to fusion of residual 'guest' material. Thus the extract residue or 'host' component of brown coals (considered to be lignin-derived) has no significant fusion event on heating to pyrolysis temperatures at 4 K/min. This is consistent with it being a highly crosslinked macromolecular solid.

The M_2T pyrograms of two nominally sub-bituminous coals are recorded in Figure 1. The thermal behaviour of the lower rank Collie specimen (74.4% C) (c) is similar to that of a brown coal containing little extractable 'guest' material but its fusion is shifted to higher temperatures than that of the brown coals. The higher rank Amberley specimen (80.2% C) (d) clearly shows two fusion transitions. The first parallels that of the Collie coal until the second sharp transition occurs above 600 K. This coal has a high liptinite content (18 vol%) and a correspondingly high hydrogen content. Its high volatile matter value (47.3%daf) ranks it as a sub-bituminous coal but its carbon rank (80.2% C daf) is indicative of a lower rank bituminous coal. The second fusion transition is characteristic of lower rank thermoplastic bituminous coals but this coal has a crucible swelling number of only 2.

The high-volatile Liddell bituminous coal (Figure 2(e)) shows little indication of thermally activated molecular mobility below 500 K. There is some fusion between 500 and 600 K followed by a major fusion transition above 600 K which appears very similar to the high temperature transition of the Amberley coal. This Liddell coal, however, has only 6% liptinite, has a crucible swelling number of 6.5 and exhibits considerable Gieseler fluidity. We therefore identify this high temperature fusion event with the aromatic-rich macerals of the coal and associate it with the thermoplastic phenomenon. Hence, by implication, a stage has been reached in the coalification processes whereby aromatic-rich material becomes fusible.

The medium-volatile bituminous Bulli coal which contains no liptinite and has significant thermoplastic properties has a M_2T pyrogram (f) showing only one fusion transition which is lesser in extent and shifted to higher temperatures than that of the Liddell coal. This transition is, of course, attributed to aromatic-rich macerals.

The M_2T pyrogram for the Baralaba low-volatile semi-anthracite (89.7% C) (g) shows this material to be totally infusible on heating to pyrolysis temperatures.

Statistical analyses were applied to the M_2T data for the 120 coals in sets (a) and (b) and for those swollen with pyridine to estimate values of this parameter for 'pure average' vitrinite, inertinite and liptinite maceral groups. It was assumed that interactive effects between macerals can be neglected and hence that M_2T varies linearly with maceral composition, i.e.

\[ M_{2T} = a \times \text{vitrinite content} + b \times \text{liptinite content} + c. \]

The regression coefficients a, b and c provide calculated M_2T values for 'pure' vitrinite (= 100 * a + c), 'pure' inertinite (=c) and 'pure' liptinite (= 100 * b + c). Because the liptinite contents span a limited range of values, extrapolations to 100% liptinite are much less reliable than those to 100% vitrinite or inertinite.
By applying this analysis at discrete 10 K temperature intervals to the NMR thermal analysis data for the 120 coals in sets (a) and (b) (subdivided into sub-bituminous and brown coals (<80% C), lower rank (80-85% C) and higher rank (85-89% C) bituminous coals), regression coefficients as functions of temperature and hence statistical M pyrograms representative of the three maceral groups were generated (Figures 3-5). Because these pyrograms are derived statistically from data on coals with a range of thermal properties and whose petrographic specifications are subject to considerable experimental uncertainty (25), they are quantitatively imprecise and can be interpreted only in a broad qualitative manner.

The 'pure' vitrinites representative of both bituminous coal subsets remain thermally stable before the onset of fusion at temperatures above 600 K and have approximately the same maximum extent of fusion (minimum $H_{MT}$) (Figures 4 and 5). The region of greatest fusion is shifted to higher temperatures for the higher rank bituminous coal subset, consistent with the expected rank dependence of coal thermostability (e.g. refs. 26 and 27). (This is better demonstrated by the plot of the temperature of maximum fusion (i.e. minimum $H_{MT}$ value) versus mean maximum vitrinite reflectance $R_{v,max}$ for the individual coals of the set (Figure 6)).

The $H_{MT}$ pyrograms for the 'pure' inertinites representative of the two lower rank coal subsets (Figures 3 and 4) indicate little molecular mobility in the temperature region of coal thermostability (i.e. $\sim$ 700 K). However, the well-defined minimum in the corresponding pyrogram for the higher rank bituminous coal subset reveals a degree of fusibility of inertinites in these coals.

The much greater fusibility of the liptinites macerals compared to the aromatic macerals for all ranks is clearly demonstrated by the results shown in Figures 3-5. The low temperature fusion of the sub-bituminous liptinites is similar in profile to that of the brown coal (Figure 1(a)), consistent with these liptinites containing the 'guest' materials extractable from brown and other low-rank coals (28). The greater thermal stability indicated by the much higher fusion temperatures of the bituminous liptinites can be explained in terms of these materials having a more highly crosslinked macromolecular structure than the liptinites in the brown coals.

Because liptinites comprise only a small fraction of most Australian bituminous coals, their contribution to the fusibility of the whole coals is expected to be minor. Thus, the $H_{MT}$ pyrograms for typical bituminous whole coals (Figure 2(e) and (f)) closely reflect the thermal behaviour of the aromatic-rich macerals.

Solvent Destabilization Data

The destabilization of bituminous coal structures due to exposure to pyridine is measured by the percentage change (decrease) in the value of $H_{MT}$ ($\Delta M_{pyr}$) for the coal after two months soak. In interpreting the results for $\Delta M_{pyr}$ we seek to isolate the separate influences of rank and maceral composition. When $\Delta M_{pyr}$ for all the coals is plotted against vitrinite content (Figure 7), there is wide scatter and no recognizable trend. However, if the coals are separated into high (>86% C) and low (80-86% C) rank bituminous subsets (Figure 7), a strong dependence on vitrinite content for the lower rank subset becomes apparent - the greater the vitrinite content the greater the pyridine destabilization. The implication that vitrinite macerals are destabilized by pyridine to a greater extent than the other maceral types is confirmed by statistical extrapolation of the $\Delta M_{pyr}$ values to 'pure' macerals by means of a linear regression analogous to that given by Equation 1 (results not presented here).

From Figure 7 it is also apparent that within the bituminous range the lower rank coals are destabilized by exposure to pyridine much more readily than the higher rank coals. Indeed, some higher rank specimens containing $\sim$80 H-wt% vitrinite are little influenced by prolonged exposure (Figure 7). This rank...
effect becomes clear when $\Delta M_{\text{pyr}}$ is plotted against $R_{\text{vmax}}$ for the vitrinite-rich specimens ($>60\%$ wt% vitrinite) (Figure 8). Above $R_{\text{vmax}} \approx 1.0$ the vitrinites become increasingly impervious to pyridine destabilization and it is only a minor effect when $R_{\text{vmax}} > 1.5$.

**Comparison of Thermal and Pyridine Destabilization**

The relationship between the extent of thermal destabilization of the molecular structures of vitrinite-rich bituminous coals on the one hand and pyridine solvent destabilization on the other is illustrated in Figure 9 in which the ratio of the decrease in $M_{\text{T}}$ during heating to the temperature of maximum extent of fusion to the pyridine-induced decrease $\Delta M_{\text{pyr}}$ is plotted versus $R_{\text{vmax}}$. For coals with $R_{\text{vmax}} < 1$ this ratio is independent of rank and its value of 1.5 - 2 (except for certain coals with relatively high liptinite contents which therefore enhance their overall fusibility) suggests (but does not require - see below) an appreciable commonality between the parts of the coal structure that are destabilized by solvent and by thermal treatment respectively. At higher rank this ratio tends to increase with $R_{\text{vmax}}$, reflecting the reduced ability of pyridine to penetrate and destabilize molecular structures which are, however, thermally destabilized at high temperatures.

**SUMMARY DISCUSSION**

Two distinct types of fusible materials occur in coals. One type is aliphatic-rich and associated with the liptinite macerals and the other is contained in the aromatic-rich macerals and particularly the vitrinites of bituminous coals.

In the case of low rank brown coals the aliphatic-rich extractable material fuses at temperatures well below 600 K. With increasing coalification rank the thermal stability of this liptinite material increases and the temperature range of its fusion transition approaches that of the thermoplastic phenomenon of bituminous coals. The enhanced stability with increasing rank is attributed to progressive covalent crosslinking which also would make the material non-extractable. In the fused state it would remain a crosslinked 'rubbery' material resistant to solvent swelling and shear-induced flow.

Fusion in the aromatic-rich macerals is the basis of coal thermoplasticity and its occurrence in effect defines the bituminous range. Fusion within the aromatic-rich structures of low-rank sub-bituminous coals is inhibited by their high covalent crosslink density. With further coalification these crosslinks are degraded and there is loss of other functional side groups. A consequence of these processes is the consolidation of the aromatic units into microdomains or micelles (7) with increasing graphite-like order. These microdomains, stabilized by London forces, are initially small and poorly ordered. With increasing rank they become larger, more ordered and increasingly stable so that their fusion temperature rises. Thermoplasticity ceases in anthracites when these physically stabilized structures achieve a degree of stability which inhibits their fusion below their temperature of pyrolytic decomposition. This stabilization process is greatly accelerated by the rapid condensation and growth in size of the aromatic units forming the ordered domains at carbon rank > 87% (29).

Of the aromatic-rich macerals the behaviour described above is most characteristic of the vitrinites. Inertinites are in general more oxygenated and aromatic than their corresponding vitrinites. Their much greater thermal stability and resistance to pyridine destabilization must relate to greater covalent crosslink density at all stages of coalification and this would also inhibit the development of the ordered microdomains in inertinites compared to that in the vitrinites.
ACKNOWLEDGEMENTS

Support was provided under the National Energy Research, Development and Demonstration Program (NERDDP). T.P. Maher of the Joint Coal Board provided coal specimens and expert advice. Maceral concentrates were provided by N. Lockhart, C. Davies, M. Shibaoka, N. Ng and A. Cook. N. Thomas and Z. Lauks performed most of the thermal analysis experiments.

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TABLE 1 Analytical data for representative coals

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<th>Coal description</th>
<th>moist. (%ad)</th>
<th>ash(%db)</th>
<th>VM(%daf)</th>
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<th>H</th>
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<th>R_{\text{max}} (%)</th>
<th>Vit. (%mff)</th>
<th>Lipt. (%mff)</th>
<th>CSN</th>
<th>Diesel</th>
<th>log (max fluidity, ddpm)</th>
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<tr>
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nd = no detectable movement
Fig. 1 $M_{2T}$ pyrograms of a brown coal (R30) (a), its extracted residue (b), and a sample of Collie (c) and Amberley (d) subbituminous coal. Analytical data in Table 1.

Fig. 2 $M_{2T}$ pyrograms of a high-volatile bituminous coal (e), a low-volatile bituminous coal (f) and a semi-anthracite (g). Analytical data in Table 1.
Fig. 3 Pyrograms of 'pure' exinite (triangles), vitrinite (o) and inertinite (x) for coals with < 80% carbon (daf).

Fig. 4 Pyrograms of 'pure' exinite (triangles), vitrinite (o) and inertinite (x) for coals with 80-85% carbon (daf).

Fig. 5 Pyrograms of 'pure' exinite (triangles), vitrinite (o) and inertinite (x) for coals with 85-89% carbon (daf).

Fig. 6 Plot of the temperature of maximum degree of fusion (TM2t(min)) against reflectance (Rmax) for bituminous coals.
Fig. 7  Plot of δMpyr against vitrinite content (on a wt% hydrogen basis) for bituminous coals with 80-86% C (○) and >86% C (x). The line of best fit to these data for the lower rank subset is shown.

Fig. 8  Plot of δMpyr against Rx,max for vitrinite-rich (>60 H-wt% vitrinite) bituminous coals.

Fig. 9  Plot of the ratio of the decreases in M2T due to heating and to exposure to pyridine against Rx,max for vitrinite-rich (> 60 H-wt% vitrinite) bituminous coals.
SPIN DIFFUSION AND SELECTIVE EXCITATION NMR TECHNIQUES
FOR COAL STRUCTURE STUDIES

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Amoco Oil Research Department
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ABSTRACT

The use of selective excitation NMR technique using DANTE pulse sequence is presented as a method to obtain higher resolution in the CP/MAS spectrum of coals. This technique is shown to work very well in isolating narrow individual resonance lines from otherwise broad NMR bands usually obtained for coals. Study of carbon spin diffusion is also discussed as a means of obtaining structural information on coals. The feasibility of observing carbon spin diffusion in coals with spin labelling and matching of magic angle spinning frequency with the chemical shift difference is discussed. This method is suggested as a possible means to derive aromatic-aliphatic carbon connectivity information.

INTRODUCTION

Solid state $^{13}$C NMR is widely accepted as an important analytical technique for coal characterization. The extent of structural information available from solid state NMR experiments on coals is, however, limited. A typical cross-polarization/magic angle spinning (CP/MAS) spectrum of coals shows two broad lines, often without much fine structure, attributed to unsaturated and saturated carbons. It is well known that the nature of NMR line broadening in coals is mainly inhomogenous, i.e., extensive overlap of resonance lines occurs due to a distribution of slightly different carbon structure types (1). It is often desirable to determine the number of unique lines that comprise the broad band as an important step for elucidating the structural features of these materials. Due to inhomogeneous nature of line-broadening, not much gain in resolution is expected by obtaining the spectrum at higher magnetic field strength. An approach to achieving higher resolution is proposed here with the use of selective excitation pulse techniques (2). A series of experiments are performed to resolve the broad band into unique resonance lines. A set of such experiments can be used to reveal extended information previously obscured by overlap.

Another experiment which can provide useful information on coal structure is the study of carbon spin diffusion. Several studies reported previously have used carbon and proton spin diffusion under favorable circumstances to obtain information on the domain size in heterogenous solids (3), intimacy of mixing in polymer blends (4) and carbon-carbon connectivities in amino acids (5). Spin diffusion between spectrally resolved carbons (also refered to as spectral spin
Diffusion is induced largely via the homonuclear dipolar coupling. The diffusion rate is thus dependent upon the internuclear distance through the strength of their dipole-dipole coupling. Observing carbon spin diffusion in coals, however, is extremely difficult due to the statistical distribution of C-12 and C-13 isotopes which renders average dipole-dipole coupling to be 10-15 Hz and thus spin diffusion rate is very slow (.1 to .01 s⁻¹). Spin diffusion rate is further reduced by magic angle spinning and coupling of carbons with the protons. Therefore, to observe carbon spin diffusion in coals very long mixing time (1-100 s) with proton decoupling field kept on is required. This places an excessive demand on the instrument performance, but more importantly the spin lattice relaxation times can compete with spin diffusion rate, making the experiment impossible. In this paper we show that it is feasible to observe carbon spin diffusion in coals by a combination of spin labelling and adjusting the rotor spinning frequency to be equal to the chemical shift difference (in Hz) of two resonance lines. This work is primarily inspired by recent articles on rotation enhanced spin diffusion in dilute spin systems by Ernst and co-workers(6) and Veeman and co-workers(7). They have shown that under the conditions of rotary resonance, spin diffusion rate can be enhanced by an order of magnitude. With this condition fulfilled spin diffusion between aromatic and aliphatic carbons in coals can be observed in as short a time as 80ms.

**EXPERIMENTAL**

The experiments were performed on a Chem-Magnetics M-100 spectrometer operating at carbon frequency of 25.11 MHz. Normal spectrum acquisition employed cross-polarization contact time of 1 ms with magic angle spinning. The spinning rate could be monitored with a tachometer during the experiment. The spinning rates were stable within 5 Hz.

Selective excitation experiment proceeds as follows: cross-polarization is used to produce transverse carbon magnetization. A non-selective 90° pulse then restores the magnetization along the external magnetic field direction. DANTE (2) (delays alternating with nutation for selective excitation) pulse sequence is then used to selectively convert a single resonance line back to the transverse plane which is then detected under high power proton decoupling. DANTE pulse sequence was a series of 20 pulses of 0.3 microsec. long (corresponding to a 90° degree non-selective pulse of 6.5 microsec. duration). 100 - 200 microsec. delays were inserted between the pulses to perform chemical shift selectivity. An approximate analysis indicated that 85% of the original intensity could be detected. Interference of DANTE pulse sequence with magic angle spinning did not present any severe problems.

Spin diffusion experiment employed the spin-exchange pulse sequence described in detail by Maciel and co-workers(8). High power proton decoupling was applied during the entire experiment. A sequence of spectra obtained for 20 analysis were transferred to a VAX computer. The 2D data was processed in a standard way. The results are presented as a 2D contour plot.
RESULTS AND DISCUSSION

Application of selective excitation and rotation enhanced spin diffusion are illustrated here with a sample of Ill#6 coal which has been labelled with C-13 enriched methyl groups at various reactive sites. Figure 1A shows the CP/MAS spectra of this sample. Two intense peaks in the aliphatic region of the spectrum correspond to the enriched methyl groups. These have been labelled as O-CH₃ and C-CH₃ indicating methyl groups which are bonded to oxygen and carbon respectively. Figure 1B-G shows the application of DANTE pulse sequence in isolating unique methyl resonance lines. The spacing between the pulses in DANTE sequence was adjusted in successive experiments in small increments to cover the full chemical shift range. Peaks representing unique chemical shifts were then selected to indicate the number of distinct methyl groups comprising the broad line. With this procedure only two unique resonance lines could be identified for the O-CH₃ groups occurring at 55 and 57 ppm whereas seven distinct peaks were isolated for the C-CH₃ groups ranging from 16 ppm to 33 ppm (not all peaks are shown in the figure). As an example of the resolution, notice in figure 1D that three lines which are within 5 ppm can be distinguished. Such fine structure would otherwise have been obscured by overlap.

The width of the narrow lines obtained with the use of DANTE sequence approach the values that are typically obtained for resolved resonance lines from a polycrystalline pure compound in a CP/MAS experiment. Line-widths of the individual lines are in the range of 1-2 ppm, which is, therefore, the limit of chemical shift resolution that can be achieved.

The ability to isolate single narrow lines affords the possibility of applying other NMR techniques to identify the chemical nature of carbons giving rise to these lines. For example, use of proton multiple pulse instead of high power decoupling during detection of single lines would result in a spectra that is indicative of the number of protons attached to the carbon (J-spectroscopy) (9). Analysis of such dipolar spectra can establish the identity of each chemical shift as from methyl, methylene, methine or quaternary carbon.

Figure 2 shows a 2D contour plot for the spin exchange experiment on the same Ill#6 coal. The purpose of the experiment depicted here was to ascertain the feasibility of observing carbon spin diffusion in coals. The off-diagonal ridges in the 2D plot indicate the chemical shifts that have participated in the spin exchange process during the mixing time. For the spin exchange to occur between two carbon atoms, they must necessarily be in close proximity to each other. Since it was unknown prior to the experiments which pair of resonance lines would satisfy such conditions, the spinning speed was set to 2630 Hz which corresponds to the chemical shift difference (in Hz) of the highest point of the C-CH₃ band and the highest point of the aromatic band. This was done with the assumption that the C-13 enriched methyl groups directly attached to the aromatic ring structure would have the greatest probability of undergoing spin exchange with the aromatic carbons.

Spin diffusion is enhanced for those carbon spins whose chemical shift differences are matched by the spinning frequency (6,7). To derive structural parameters from such experiments, a series of 2D experiments would have to be performed covering full shift range of aromatic and aliphatic carbon band.
Alternatively it is possible to derive the same information in less time by 1D NMR with the use of DANTE sequence as demonstrated by Ernst and co-workers[6] for pure model compound.

The study of spin diffusion is an extremely promising technique for obtaining structural information about spatial positions of carbon atoms in solids[10]. In particular, rotation enhanced spin diffusion appears to be a well suited technique to study the aromatic-aliphatic carbon connectivities in coals. With an appropriate choice of mixing time, it should be possible to discriminate between pairs of carbon atoms as directly bonded or two or more bonds away, i.e., aliphatic carbons alpha to the aromatic ring versus others.

ACKNOWLEDGEMENTS

Technical assistance of members of analytical NMR group at Amoco Research Centre is gratefully acknowledged. Special thanks also go to Dr. Joseph T. Joseph of Amoco Oil Company for providing the C- and O- alkyalted Ill#6 coal sample.

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Figure 1: Application of DANTE pulse sequence to isolate individual components of the C-13 enriched O-CH₃ and C-CH₃ groups. See text for details.
Figure 2: Absolute mode two dimensional contour plot for spin exchange with 80 ms mixing time for labelled I11#6 coal. Spinning frequency = 2630 Hz. Markings on the axis are in ppm. See text for details.
DETERMINATION OF NITROGEN AND SULPHUR FUNCTIONALITY IN COAL AND COAL LIQUIDS


INTRODUCTION

The type and distribution of nitrogen and sulphur functional groups in raw coal and their fate during processing have vital implications for the environmental impact of coal utilisation, as well as for the mechanism of the processes themselves. The combustion of nitrogen and sulphur rich fuels is known to release many hetero-PAC's, NO, and SO<sub>2</sub> compounds into the atmosphere. NO and SO<sub>2</sub> can be formed from the oxidation of nitrogen and sulphur compounds present in the fuel and, in the case of NO<sub>2</sub>, also from atmospheric nitrogen (thermal NO<sub>2</sub>). Whilst conventional petroleum derived fuels contain low enough heteroatom concentrations for thermal NO<sub>2</sub> to predominate, in typical liquid fuels derived from coal, which have much higher heteroatom contents, fuel derived NO and SO<sub>2</sub> are dominant. Furthermore, combustion of fuel bound nitrogen under fuel rich conditions can lead to the formation of HCN and NH<sub>3</sub>, as well as NO.<br>
The ultimate fate of the nitrogen and sulphur functional groups in coals and coal derived liquids is, however, dependent on the types of functional groups in which they are present. Non-basic nitrogen functions are thought to be the major source of NO emissions during combustion whilst reactive sulphur compounds, such as mercaptans, cause excessive metal corrosion during processing. In addition, some nitrogen and sulphur compounds (e.g. nitrogen bases) are known to reduce the useful lifetime of the catalysts used during the refining processes<sup>1</sup>.<br>
In this paper we report on methods which allow the analysis of nitrogen and sulphur functional groups in samples ranging from raw coals to process derived liquids and solids. X-ray photoelectron spectroscopy (XPS) has been combined with potentiometric titration and infra-red spectroscopy to provide a self consistent quantitative analysis of nitrogen functionality. Sulphur functional group distributions have been determined by temperature programmed reduction (TPR) and the method has been applied to study the hydrogen donor liquefaction of coal. The potential of using XPS as a method for the study of sulphur functional groups is also discussed.

EXPERIMENTAL

1) Materials
Two SRC process solvent residues (A, 397 °C; B, 351 °C), a coal liquid produced in a tubing bomb shaking autoclave from Burning Star coal, a Belgian (Beringen) coal and its SRC product were
studied. To facilitate nitrogen functional group determination, the samples were separated into n-pentane soluble, asphaltene and preasphaltene fractions. The asphaltenes were further separated by a fractionation scheme outlined elsewhere. The scheme produced three nitrogen-rich fractions consisting of strong bases, weak bases (as quaternary salts) and neutrals. The fractions were then analysed by the methods outlined below.

2) X-Ray photoelectron spectroscopy
Photoelectron spectra were recorded on a Kratos ES300 spectrometer using AlK$_\alpha$ radiation. The spectrometer was run in fixed analyser transmission mode at a pass energy of 65eV, slit width 1.75 mm with an X-ray source power of 300 W. Powdered samples were mounted by pressing onto double sided adhesive tape and introduced into the spectrometer via a rapid insertion probe. Coal samples were ground under heptane in a ball mill to <5um and stored under heptane before use to minimise the effects of surface oxidation. Spectra were recorded at a pressure of less than 1x10$^{-5}$ Pa. Data acquisition was controlled by a Kratos DS300 data system which was also used for spectral quantification and analysis. In order to obtain N(ls) spectra of sufficient quality to permit resolution of the different nitrogen components, long data acquisition times were required. For samples of the lowest nitrogen concentration this amounted to several hours of data accumulation. The nitrogen peak was resolved using a peak synthesis routine employing symmetric components of Gaussian line shape at fixed binding energies determined from model compound studies. The intensities of the components were varied in order to obtain the best fit to the experimental spectrum while constraining the full widths at half maximum of all the components to be within the limits 1.8 to 2.0eV.

3) Infra-Red Spectroscopy
Quantitative infra-red spectra were recorded to determine the amount of nitrogen present as non-basic N-H. Spectra were recorded on a Perkin Elmer 1750 Fourier Transform Infra-red Spectrometer. Samples were dissolved in deuterochloroform at low concentration (<30mg/10ml), to reduce hydrogen bonding, and spectra recorded in a 1 cm quartz cell.

Quantification of the N-H stretch (3460-3480 cm$^{-1}$), for fossil fuel derived samples, was achieved from a calibration graph of absorbance at this wavelength versus NH concentration determined, by XPS. In all cases samples were methylated using diazomethane before analysis to remove the interfering OH absorptions.

4) Potentiometric Titration
Non-aqueous potentiometric titration was used to determine the basic nitrogen content of soluble samples, including those samples of low molecular mass which were not amenable to study by XPS because of higher vapour pressure. Between 100mg and 500mg (depending on nitrogen content) of the sample was dissolved in a small quantity of benzene or chloroform before the addition of 50-75cm$^3$ of the titration medium, glacial acetic acid. The titrant, 0.05M perchloric acid in glacial acetic acid, was added...
via an automatic titration system and the end point detected using a combined glass and a calomel electrode.

5) Temperature Programmed Reduction

Temperature programmed reduction experiments were performed in a 3ml stainless steel reactor designed to give optimum recovery of sulphur. The samples (between 5mg and 75mg depending on sulphur content) were mixed with a reducing solvent mixture (phenanthrene, resorcinol, 9,10 dihydrophenanthrene, tetralin and pyrogallol) in the reaction vessel and sonicated for one hour. The reduction experiment was performed by fitting the reaction vessel to a stainless steel condenser arrangement and applying a temperature ramp of 7 °C/min to the cell. Any H₂S evolved was flushed from the cell by a stream of preheated nitrogen (30 ml/min) and make-up nitrogen was added (30 ml/min) to the gas stream immediately following the condenser system. The H₂S was detected by measuring the sulphide ion in an alkaline sulphur antioxidant buffer (SAOB) using a sulphur-specific electrode system. The sulphide electrode was calibrated by adding small amounts of sodium sulphide to the SAOB solution via an automatic burette. The electrode response was checked at the beginning and end of each run by adding a known concentration of sodium sulphide. Changes in the cell potential and reactor temperature were recorded by a computer data capture system and the data were subsequently output as plots of sulphur concentration versus temperature or as the integrated signal.

RESULTS AND DISCUSSION

1) Quantification of Nitrogen Functional groups

1) XPS of Nitrogen Containing Functional Groups

Table I shows the ultimate analysis data for the coal and coal derived products studied. In every case these products gave rise to a single, broad, N(1s) peak in their XPS spectra. In all cases, except for the quaternarised samples, the N(1s) spectra could be resolved into two major components at binding energies of 400.2eV and 398.8eV corresponding to nitrogen in pyrrole and pyridine type structures respectively. The proportions of the two components were calculated for each fraction and are shown in Table I. The XPS spectra of the fractions quaternarised with methyl iodide are more complex since the reaction produces a pyridinium ion

\[ \text{N} + \text{CH}_3\text{I} \rightarrow \text{N}^+\text{CH}_3\text{I}^- \]

This produces a shift in the pyridine N(1s) binding energy from 398.8eV to 401.4eV and the associated iodine concentration provides a further quantification of the pyridine groups. Since the pyridinium ion is unstable in the X-ray beam, however, the N(1s) spectrum consists of four components. From model compound studies using quaternarised phenanthridine, these were found to be, in order of decreasing binding energy, the quaternary salt
(401.4eV), pyrrole types (400.2eV), the degradation peak (399.5eV), and a small component due to residual pyridine types. The peak synthesis is simplified, however, because the quaternary and degradation product peaks are coupled and their ratios may be determined by analysis of the I(3d₃⁄₂) peak. The result of N(1s) peak synthesis on the quaternarised Burning Star asphaltene is shown in Figure 1. The amount of pyridinium ion calculated from the iodine peak is in excellent agreement with that calculated by N(1s) peak synthesis alone, validating the N(1s) peak assignments. As a check of the XPS results, the basic nitrogen contents of some of the asphaltene fractions were determined by potentiometric titration. The amount of basic nitrogen determined directly agrees well with the XPS results (correlation coefficient 0.95), further confirming the validity of the XPS procedure. XPS, however, unlike the titration method, is not limited by the solubility of the samples.

**ii) Infra-Red Spectroscopy**

Since a simple two component model was found to fit the XPS data for all samples, the pyrrole to pyridine ratios obtained in this way can be viewed with some certainty. The volatile nature of some of the lower molecular mass coal derived fractions, however, makes them difficult to study by XPS. Because of this, the pyrrole contents, as determined by XPS, were used to calibrate the infra-red NH stretch (3480 cm⁻¹). Figure 2 shows the plot of absorbance versus the XPS determined NH concentration for the range of coal derived asphaltene fractions studied. Several of the samples were recorded over a range of concentrations to establish the validity of the Beer-Lambert relationship for these materials. The linearity of these plots indicates that the solutions were sufficiently dilute to prevent significant intermolecular hydrogen bonding. Using the Beer-Lambert law the specific absorption coefficient per gram of NH was calculated to be 6.9 ± 0.4 dm³g⁻¹cm⁻¹. With this value it is possible to use infra-red spectroscopy as an independent method of calculating [NH]. Furthermore, comparison of the XPS and FT-IR data obtained from shale oil asphaltene suggests that the extinction coefficient may be generally applicable to high molecular mass fossil fuel samples.

**2) Analysis of Sulphur Containing Functional Groups**

**i) Temperature Programmed Reduction of Sulphur Functional Groups**

The Beringen coal and its SRC product were analysed by temperature programmed reduction (TPR). The TPR kinetogram of the coal showed two resolved peaks at 380°C and 420°C, corresponding to the reduction of organic sulphur functional groups and pyrite respectively. In contrast to this, the TPR kinetogram of the SRC product obtained from the same coal contained no pyrite peak and the peak due to the reduction of the organic components was shifted to lower temperatures, consistent with a change in sulphur functional group distributions. From model compound data, this peak shift suggests the formation of aromatic sulphide groups from thiophene structures.
ii) XPS of sulphur containing functional groups

Since XPS can analyse for all elements except hydrogen and helium, it offers a potential method for the determination of sulphur functional groups in fossil fuels. Frost et al\textsuperscript{7} and Perry and Grint\textsuperscript{8} demonstrated that there was a correlation between surface and bulk sulphur contents over a range of coals. XPS has also been applied to study of sulphur in diesel particulates\textsuperscript{9}, and, more recently, to determine the role of sulphur compounds in liquid fuel stability\textsuperscript{10}.

Analysis of the S(2p) spectra of the coal-derived samples discussed in section 1 above reveals that in most cases sulphur is present in one valence state, with binding energies centred at between 162.4 eV and 164.7 eV, depending on the individual sample, and corresponding to various organic sulphur (II) types (i.e. thiols, sulphides, disulphides or thiophenes). As shown in Figure 3a, however, in some samples, two peaks were observed, one centred at 164.5 eV and the other at 169.3 eV. These correspond respectively to organic sulphur (II) and oxidised sulphur (IV and VI) species. Comparison of the binding energy of the oxidised sulphur peak (169.3 eV) with those for model compounds\textsuperscript{11-13} reveals that this peak is probably due to sulphones (R-SO\textsubscript{2}-R).

Jones et al\textsuperscript{11} showed that the performic acid/methanol oxidation of thiophene structures yields sulphones in a two step process which goes via the sulphoxide. The sulphur peak at 169.3 eV may, therefore, be tentatively assigned to the oxidation products of thiophenes (or sulphides) in the original asphaltene.

From consideration of the chemical shift data for sulphur containing model compounds, it is apparent that the chemical shift range for the possible fossil fuel sulphur types is not as great as was observed for nitrogen species. Furthermore, the larger number of possible functional groups would complicate the analysis. It is unlikely, therefore that a simple analysis by peak synthesis methods will be as effective as it was for nitrogen functional groups. As sulphur can exist in several different stable oxidation states, however, there is a potentially greater S(2p) chemical shift range accessible. Figure 3b shows the S(2p) spectrum of the SRC asphaltene 'A', after reaction with methyl iodide in which sulphur (I) is converted to sulphur (IV). As with the nitrogen compounds, an obvious peak shift to higher binding energies is evident. This shift is consistent with the formation of a sulphonium salt of the form RR'S'Me I. Clearly, derivatisation reactions of this type can be readily applied to the S(2p) of sulphur in combination with a suitable fractionation scheme, or a series of selective derivatisation/oxidation reactions, it will provide a method from which valuable information about the distribution of sulphur types in coal and its derivatives may be obtained.

ACKNOWLEDGEMENTS

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REFERENCES

TABLE I
Distribution of Nitrogen Functional Groups

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<tr>
<td>H</td>
<td>6.9 7.1</td>
<td>6.2 6.2</td>
</tr>
<tr>
<td>N</td>
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<td>2.5 6.7</td>
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<td>- -</td>
<td>- -</td>
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<tr>
<td>H/C</td>
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<td>0.90 0.94</td>
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<tr>
<td>N/C</td>
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<td>0.03 0.07</td>
</tr>
<tr>
<td>% Pyrrolic</td>
<td>62 30</td>
<td>49 35</td>
</tr>
<tr>
<td>% Pyridinic</td>
<td>40 62</td>
<td>50 63</td>
</tr>
</tbody>
</table>
Figure 1. Synthesised N(1s) Spectrum of the Quaternarised Burning Star Asphaltene

Figure 2. Plot of Absorbance Versus [NH] (Determined by XPS) for a Range of Coal Derived Asphaltene Fractions
Figure 3. S(2p) Spectra of a) Asphaltenes and b) Quaternarised Asphaltenes
DIRECT DETERMINATION AND QUANTIFICATION OF SULFUR FORMS IN HEAVY PETROLEUM AND COALS. PART I: THE X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) APPROACH

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Abstract

We have used the results from model compound studies to deconvolute the sulfur 2p signal from coal and heavy petroleum samples in the terms of the amounts of alkyl sulfides (163.3 eV) and thiophenic-like (164.1 eV) forms. The determination of organic sulfur forms in Illinois #6 coal was accomplished by carefully monitoring the contributions due to iron sulfides and sulfates and application of the deconvolution procedure used with heavy petroleum samples. Our results show that thiophenic-like sulfur comprises the majority of organic sulfur species in fresh Illinois #6 and Rasa coal. Analysis of Rasa coal following air oxidation show that organic sulfidic forms are much more reactive toward oxidation than thiophenic-like species.

I. Introduction

The routine direct quantification of organic sulfur forms in solids and nonvolatile liquids has not yet been accomplished; however, progress has been made using X-ray Adsorption Near Edge Structure (XANES) (1-2). The capability is important for understanding the chemistry of sulfur in coal and heavy hydrocarbons. It has been long recognized that XPS could potentially impact this characterization area for coal (3-0). The characterization of sulfur on coal surfaces by XPS is complex due to the presence of pyrite and other inorganic sulfur species. Other complications are that both organic and inorganic sulfur forms are susceptible to ambient oxidation and that the surface composition may not be representative of the bulk. Despite this awareness there has been very little detailed attention paid to contribution of inorganic sulfur forms. An XPS study (7) of many different coals observed only trace iron signals. The authors associated the 164.2 eV sulfur 2p peak with organic sulfur and attributed it to the sum of thiophenes, sulfides and mercaptans. This study (7) also demonstrated a reasonable correspondence between surface and bulk organic sulfur levels. Our approach to avoid the problems posed by the presence of inorganic sulfur was to establish XPS methods for quantitative determination of sulfur forms using model compounds and petroleum based materials. The same methods were then applied to a coal with a low pyrite and high organic sulfur content for characterization of sulfur forms. Finally a coal with equivalent amounts of pyrite and organic sulfur was analyzed for organic sulfur species after accounting for the contribution of inorganic sulfur forms to the XPS sulfur 2p signal.

II. Experimental

Illinois #6 coal was obtained from the Argonne premium coal sample program. The Rasa coal sample was obtained courtesy of Dr. Curt White at the Pittsburgh Energy Technology Center PETC. Polyphenylene sulfide was obtained from Scientific Polymer Products Inc. and all other model compounds were obtained from the Aldrich Chemical Company, Inc. XPS spectra were obtained with a Vacuum Generators ESCALAB instrument using non-monochromatic MgKα or AlKα radiation.
The petroleum samples were deposited from solution onto a metallic sample block. The coal and powdered model compound samples were mounted to the metallic sample block by means of double sided nonconducting tape. An energy correction was made due to sample charging for coal based on the C(1S) peak position observed at 284.8 ± 0.1 (eV) for the thin films (<10Å thickness) of heavy petroleum samples and THF extracts from Illinois #6 samples. These samples are believed to be in electrical contact with the metallic sample block. The spectra were obtained at 0.9 eV resolution. Data acquisition and processing were by means of the VGs 2000 software package. Oxidation experiments were done in air with ~60% relative humidity.

III. Results and Discussion

An idealized XPS sulfur 2p signal is made up of 2p3/2 and 2p1/2 components having 2:1 relative intensity and separated in energy by about 1.2eV. We have measured the XPS sulfur 2p signal from a variety of model compounds to obtain the instrumental response for a single component species as well as determine the binding energy representative of different sulfur environments. Figure 1 shows the spectra from several model compounds. We have found that the sulfur 2p signal can be represented by components having an equally mixed Gaussian-Lorentzian line-shape and a FWHM of 1.4 eV. Figure 1 curves A, B and E are examples which have this idealized line-shape. There is a very small peak at several eV higher binding energy than the main 2p signal in curves A and B. This emission is primarily a result of $\pi - \pi^*$ shake-up processes (9). We can identify departures from what would be expected for a pure component material. There is a slight broadening of the sulfur 2p signal in Curve C for 2-methyl-L-cysteine; however, the sample is only of 97% purity. The broadening of the higher binding energy peak from the partially oxidized FeS2 sample, curve D, reflects the presence of oxidized sulfur in environments with slightly different apparent binding energy.

The XPS sulfur 2p binding energy provides a sensitive measure of the electronic character of sulfur within a molecule. The binding energies of oxidized organic sulfur forms are fairly well established (8-14) i.e., sulfoxides -(166 eV), sulfones -(168 eV) and sulfonic acid/sulfate -(169 eV). Figure 1 curve E is the sulfur 2p spectrum from dibenzothiophene sulfone which shows a binding energy 168.2 ±0.1 eV. This agrees favorably with the values reported for sulfone in different polymeric materials (9). The details of the surface oxidation of FeS2 are complex and will be discussed in greater detail later. The sulfur 2p spectrum of partially oxidized FeS2 is shown in Figure 1 curve D. The lower binding energy peak occurs at 162.5 eV and is consistent with previously reported values for pyritic sulfur (15-19) which range from 162.3 eV to 163.0 eV. The higher binding energy peak occurs at 168.6 eV and is associated with sulfite. Sulfite was observed as a surface product following air oxidation of pyrite with binding energies of 168.5 eV (19) and 169.1 eV (16). These values are close to those anticipated for ferrous and ferric sulfite (12). Indeed we find the binding energy of ferrous sulfite at 168.9 eV. Brion (16) found 169.4 eV and 169.5 eV for ferric and ferrous sulfate respectively. Values as high as 171.0 eV and 172.2 eV have been published (4, 6) for ferric and ferrous sulfate respectively; however, no attempt was made to account for sample charging in these studies. The binding energy for polyphenylene sulfide in Curve B is 163.7 ± 0.1 eV which quantitatively agrees with a previous finding (9). The 164.1 eV binding energy for sulfur in a thiophenic-like environment (Tilorone Analogue) also agrees with that found for thiophene (12). We find a 168.3 eV binding energy for an alkyl sulfide containing...
molecule S-methyl-L-cysteine.

We have measured the XPS sulfur 2p signal from several heavy petroleum samples. The XPS sulfur 2p signal for a single species, based on the instrumental response of pure model compounds, was used in a deconvolution procedure. It was possible in all cases to deconvolute the spectrum from petroleum asphaltene samples into two signals with binding energies of 164.1 eV and 163.3 eV (23). This observation was interpreted in light of available model compound results. The 163.3 eV component is representative of mostly sulfidic forms while the 164.1 eV corresponds to thiophenic-like environments.

We have analyzed the XPS sulfur 2p signal from fresh Rasa lignite coal. The spectrum is shown in Figure 2. It is an unusual coal, having very high levels of organic sulfur (11.68 wt%) and very little inorganic sulfur. The sulfur to carbon atom ratio as determined by XPS was in excellent agreement with that determined by elemental analysis. As we found with petroleum asphaltenes, it was possible to deconvolute the main sulfur 2p peak into 164.1 and 163.3 eV components. The 164.1 eV peak makes up 70% of the signal and is assigned to organic sulfur species in thiophenic-like environments. Air oxidation for 5 days at 125°C changes the sulfur 2p spectrum as shown in Figure 3. The presence of oxidized sulfur forms is apparent at high binding energies and these forms make up about 24% of the total sulfur on the surface of Rasa coal. Upon oxidation, the amount of thiophenic-like components remains nearly constant, but the sulfidic components drop dramatically. The distribution of sulfur forms remains about the same following subsequent oxidation in air at 125°C up to 60 days. These results show that the thiophenic-like sulfur components in Rasa lignite are much less reactive toward oxidation relative to sulfidic forms.

Accounting for possible inorganic sulfur forms is essential for an accurate determination of organic sulfur surface species in pyrite containing coals. Figure 4 Curve A shows the iron 2p spectrum from Illinois #6 coal. The Illinois #6 sample was obtained from the Argonne premium sample program in a sealed ampule. The sample was prepared in an N₂ dry box, placed in a sample transference device, evacuated and then inserted into the VG fast entry air lock for XPS sample analysis. The procedure nearly eliminated exposure to laboratory air. About half of the bulk sulfur in this coal is present as pyrite. The XPS iron spectrum contains a number of peaks that will be identified on the basis of 2p3/2 and 2p1/2 components from at least two distinct chemical forms. We can identify a sharp iron 2p3/2 peak at 708.5 eV and another very broad 2p3/2 peak at 713.5 eV. The energies were determined after correction for sample charging based on the C(1S) coal peak.

Careful studies on the surface oxidation of pyrite have shown that initial air oxidation products are an iron deficient sulfide, iron oxides and/or ferric sulfate (19). The binding energy of the metal-deficient sulfide is believed to be similar to unaltered pyrite (19), -707 eV (15-19). Iron oxides and ferric sulfate occur at -711 eV. We have measured a binding energy of 711.0 eV for ferric sulfate. Sulfate was observed (19) by XPS as a later oxidation product of pyrite exposed to air. No evidence was found for the presence of elemental sulfur up to 14 day air exposure (19); however, elemental sulfur is an observed component in weathered coal samples (26).
The iron 2p3/2 binding energies from Illinois #6 coal cannot be chemically interpreted in a straightforward way because the value falls outside of known limits. To conform to accepted values, the inorganic components would have to experience enhanced sample charging of about 1.0eV to 3.0eV relative to the main organic carbonaceous components. The possibility of enhanced sample charging for inorganic components in coal has been noted before (24,25). If we assume nonuniform sample charging, then the 708.2 eV peak is assigned to iron pyrite or the metal deficient sulfide shifted by +1.2eV and the broad peak at ~713.5 eV to iron oxides and/or sulfates shifted by +2.5eV. It would follow that the ~722 eV feature is due to the 2p1/2 peak from pyrite and the broad 727eV peak due to 2p1/2 from iron oxides and/or sulfates. These results show that the substantial portion of the observable iron from a fresh sample surface of Illinois #6 coal is non-pyritic in nature and in poor electrical contact with the organic matrix.

When the XPS sulfur 2p signal from iron pyrite is shifted by 1.2eV toward higher binding energy, it will directly overlap the region for unoxidized organic sulfur species. The total amount of iron present, as determined by the combined area of the 2p3/2 peaks from all iron species relative to the total amount of carbon, is only about a third of the amount determined by bulk analysis (Fe/C = 0.0071). Lower than expected iron XPS signals have been noted before (7). Two possible explanations are that the pyrite particles are encapsulated by organic material or that they have a particle size distribution significantly greater than the carbonaceous matter. The pyritic 2p3/2 peak is only 20% of the total 2p3/2 iron signal. We would, therefore, expect a pyritic XPS sulfur 2p signal that corresponds to a relative intensity of (S/C=0.001) or about 7% of the total sulfur 2p signal. The apparent binding energy of pyritic sulfur would be 163.7 eV due to enhanced sample charging. The pyritic XPS 2p3/2 signal decreases substantially upon exposure to air. Figure 4 curve B shows the decline in the iron 2p3/2 signal and Figure 5 curve B shows the appearance of a very small sulfate peak near 171.5 eV after a two day exposure to air at 22°C and ~60% relative humidity. Pyritic sulfur is initially present in very small quantities at surfaces of fresh Argonne premium Illinois #6 samples and the amount declines further upon exposure to air.

It was possible to deconvolute the XPS organic sulfur 2p signal from Illinois #6 coal using the same methods as used with Rasa coal and heavy petroleum samples after consideration of the pyritic sulfur contributions as just described and background subtraction of the silicon 2s signal. Figure 6 shows the results. The 164.1 eV peak contributes 64% and the 163.3 eV peak 29% to the total signal. These peaks are interpreted to arise from thiophenic-like and alkyl sulfide environments respectively. These results show that organic sulfur species dominate the XPS sulfur 2p spectrum of fresh Illinois #6 coal and that about 2/3 of the surface organic sulfur exists in thiophenic-like environments.

IV. Conclusions

It is possible to deconvolute the organic XPS sulfur 2p spectrum of coal and heavy petroleum samples into 163.3 eV and 164.1 eV components. These peaks have been interpreted in terms of alkyl sulfides and thiophenic-like sulfur species respectively. Thiophenic-like sulfur represents the majority organic species in Rasa and Illinois #6 coal. Air oxidation of Rasa coal results in the loss of organic sulfides and the production of oxidized species. Detailed analysis of the iron and sulfur XPS sulfur 2p signals shows that inorganic
sulfur species represent a very small fraction of the total sulfur present on surfaces of fresh Argonne Premium Illinois #6 coal.

References


Figure 1

XPS sulfur 2p spectra from model compounds.

Figure 2

XPS sulfur 2p spectrum from fresh Rasa coal and deconvolution into 163.3 eV and 164.1 eV components.
Figure 3  XPS sulfur 2p spectrum from Rasa coal oxidized for 5 days at 125°C and deconvolution into 163.3 eV and 164.1 eV components.

Figure 4  XPS iron 2p spectra from Argonne Premium Illinois #6 coal: a) Fresh; b) after air exposure at 22°C for 2 days.
Figure 5  XPS sulfur 2p spectra from Argonne Premium Illinois #6 coal; a) Fresh; b) after air exposure at 22°C for 2 days.

Figure 6  XPS sulfur 2p spectrum from fresh Illinois #6 coal and deconvolution into different components.
DIRECT DETERMINATION AND QUANTIFICATION OF SULFUR FORMS IN HEAVY PETROLEUM AND COALS. PART II: THE SULFUR K EDGE X-RAY ABSORPTION SPECTROSCOPY APPROACH

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Annandale, NJ 08801

ABSTRACT

A Sulfur K Edge X-ray Absorption Spectroscopy method has been developed for the direct determination and quantification of the forms of organically bound sulfur in nonvolatile petroleum and coal samples. XANES spectra were taken of a number of model compounds, mixtures of model compounds, heavy petroleum and coal samples. A third derivative analysis of these spectra allowed approximate quantification of the sulfidic and thiophenic components of the model mixtures and of heavy petroleum and coal samples.

INTRODUCTION

Although many attempts have been made to determine the forms of organically bound sulfur in nonvolatile and solid hydrocarbonaceous materials, virtually all have involved in one way or another some chemical change to the structures, and leave open questions as to what is being measured (1). While less of an issue for petroleum based samples (2), chemical derivatizations of coal require good mass transport to be sure that the reaction is complete and all products are accounted for. Pyrolysis type experiments (3a) leave open the question as to whether sulfur forms are interconverting (3b). To remove these ambiguities, a direct measurement is required, which must be element specific, environment sensitive, and must be able to observe the entire sample. X-ray Absorption Spectroscopy (XAS) is one such method. In earlier work Hussain et al. (4), Spiro et al. (5), and later Huffman et al. (6,7) demonstrated the potential of sulfur X-ray absorption spectroscopy for the qualitative determination of sulfur forms in coals, however they made no attempt at quantification. This report investigates the applications of X-ray absorption near edge spectroscopy (XANES) for the purpose of speciating and quantifying the forms of organic sulfur in solids and nonvolatile liquids.

EXPERIMENTAL SECTION

The details of the XANES experimental setup and data analyses have been described previously (3b,8). All model compounds used in this study were obtained from Aldrich Chemical Company and were used without further purification. The asphaltene samples were prepared from their respective petroleum residua by precipitation from n-heptane following the procedure of Corbett (9). A sample of Rasa lignite was generously provided by Dr. Curt White. The sample of Illinois #6 coal was obtained from the Argonne Premium Coal Sample Bank.

RESULTS AND DISCUSSION

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XANES of Model Compounds

Table 1 lists the first inflection points of the sulfur K edge spectra for a series of model compounds whose structures are believed to be representative of the types of organically bound sulfur found in heavy petroleum and coals. Although the absolute value for the energy calibration contains some uncertainty, the relative accuracy of the energy scale proved to be reproducible to within less than 0.1 eV. The total span in energy is quite large, being some 12.4 eV between thiohemianthraquinone and potassium sulfate. As might be anticipated (10,11), the first inflections of compounds with more oxidized sulfur are notably higher in energy than for those with reduced sulfur. The sulfur XANES spectra of compounds with similar sulfur electronic environments were found to be similar. For example, dibenzothiophene and benzothiophene were found to give similar sulfur XANES spectra, whereas dibenzothiophene and thiophene, whose sulfur atoms are in significantly different environments, exhibit dissimilar sulfur XANES.

Examination of Table 1 reveals that the edge of dibenzothiophene is displaced from that of benzyl sulfide, the first inflection energy being some 0.6 eV higher for the former compound. The XANES spectra of the compounds listed in Table 1 (3b,8) can readily be used as a fingerprint for the electronic nature of organically bound sulfur, and for distinguishing between the forms of sulfur in the pure compounds. From previous XANES data on dibenzothiophene and benzyl sulfide and physical mixtures of the two, it proved possible to identify each compound in the presence of the other (3b,8). Additionally by simply measuring the heights of the third derivative features at 2469.8 eV and 2470.8 eV relative to the base line in the model compound mixtures, a calibration was established which allowed an approximate estimate of the amounts of each component in hydrocarbon samples to be obtained.

XANES of Petroleum Residua

On the left side of Figure 1 the sulfur K edge spectra for three different petroleum residua and the asphaltene samples prepared from them are shown. While the three component spectra all appear to be similar, differences are revealed by examining the third derivatives of the spectra, which are shown on the right side of the figure. All the residua samples appear to contain sulfur bound in sulfidic and thiophenic forms, the amount of sulfidic sulfur increasing from sample 1 to sample 3. The asphaltene samples prepared from residua 2 and 3 also appear to contain both forms. Assuming that the composition of the sulfur forms in these samples is approximated by the simple two component mixture of dibenzothiophene and dibenzylsulfide models, an estimate of the relative molar quantities of sulfidic and thiophenic forms can be obtained as described above. These approximate values are listed in Table 2. In samples 1 and 3, it is clear that the predominant form of sulfur in the asphaltene fractions is thiophenic and the predominant form in the whole residuum is sulfidic. For sample 2, there appears to be no such discrimination.

In the latter case, the totals do not add to 100%. While thickness effects may play a role, a more probable explanation for this observation is that a range of slightly different sulfur types, of both sulfidic and thiophenic forms exist in this material, which causes a broadening of the features of the XANES spectrum and making quantification based on mixtures of two model compounds less
accurate. In agreement with this the structure of the third derivative spectra of both the resid sample 2 and the asphaltene derived from it do appear to be broadened relative to that of the spectra of sample 3 in Figure 1. Since the broadening takes place in the "sulfidic" region, both data sets were normalized to 100%, giving a rough approximation of the amounts of sulfidic and thiophenic sulfur, which are shown in parentheses in the table.

XANES of Coal

In Figure 2 are shown the XANES spectra and their third derivatives of the Rasa lignite and Illinois #6 coal samples, and Table 2 the approximate quantification of sulfur types. The former coal was chosen for this study because it has an unusually high amount of organically bound sulfur, and an unusually low level of pyritic sulfur (12). The latter was chosen because its relatively high pyritic sulfur content provides a means of defining to what extent pyritic sulfur interferes with data interpretation.

For Rasa lignite, this XANES analysis indicates that about 30% of the sulfur is sulfidic and 70% is thiophenic. These numbers are in agreement with those found by XPS (14). Partial confirmation of these values also comes from the work of Kavcic (13), who showed that about 75% of the sulfur in this lignite was not reactive toward methyl iodide; this lack of reactivity was attributed to the sulfur being bound in ring structures. Even recognizing the potential or inherent errors of the methyl iodide method such as degree of reaction, possible side reaction, etc., the extent of agreement of the direct and indirect techniques is good.

The XANES spectrum for the Argonne Premium Illinois #6 coal and its third derivative in Figure 2 clearly show that pyritic sulfur is a significant component. As a first step to extract data on the organic sulfur content, the XANES spectrum of iron pyrite (determined separately and not shown in the figure) was mathematically subtracted from the XANES spectrum of the coal. The resulting spectrum and its third derivative are shown in Figure 2 below those of the whole coal, and from this third derivative approximate quantifications of 60% sulfidic and 40% thiophenic sulfur forms were determined (Table 2). It is interesting to note that these are in reverse order from what was found by XPS analysis on this same coal (14) and on another Illinois #6 sample by pyrolysis techniques (3a). The XANES approximations for this coal should be considered as tentative and subject to change due to possible errors in the subtraction method used. For example, if the pyrite actually present in the coal has different spectral characteristics than the pyrite sample examined by XANES, the sulfidic numbers could be higher than actual. Work is in progress to better define the interference effects of pyritic sulfur. It is interesting to note that if these data are shown to be valid, comparison with data obtained by pyrolysis would imply that sulfidic sulfur can interconvert to some extent to thiophenic sulfur on heating.

CONCLUSIONS

This work has demonstrated that organically bound sulfur forms can be distinguished and in some manner quantified directly in model compound mixtures, and in petroleum and coal. The use of the third derivative XANES spectra was the critical factor in allowing this analysis. The tentative quantitative
identifications of sulfur forms appear to be consistent with the chemical behavior of the petroleum and coal samples, although large amounts of pyritic sulfur may interfere with the accuracy. Further work is in progress to resolve the pyritic sulfur question and to extend these techniques to other nonvolatile and solid hydrocarbon materials.

ACKNOWLEDGEMENTS

X-ray absorption spectra were recorded at the Stanford Synchrotron Radiation Laboratory, which is funded by the Department of Energy, under contract DE-AC03-82ER-13000, Office of Basic Energy Sciences, Division of Chemical Sciences and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. The writers wish to thank Dr. Curt White (PETC) for providing a sample of Rasa lignite, and Dr. K. Vorres (Argonne) for the sample of Illinois #6 coal.

REFERENCES CITED


### TABLE 1

Sulphur K edge First Inflection Energies (b)

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<th>Compound</th>
<th>First Inflection (a)</th>
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<td>K2SO4</td>
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<tr>
<td>anthraquinone 6-sulfonate(Na)</td>
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<tr>
<td>dibenzothiophene</td>
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<td>methionine</td>
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<td>thiohemianthraquinone</td>
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a. First inflection points were obtained from the position of the lowest energy maximum of the first derivative, and are considered accurate to better than 0.1 eV.

b. Modified from Reference 8.

### TABLE 2

Approximate Quantification of Organically Bound Sulfur Forms in Heavy Hydrocarbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Sulfidic (± 10)</th>
<th>%Thiophenic (± 10)</th>
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<td>Petroleum</td>
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<tr>
<td>Residuum 1</td>
<td>29</td>
<td>71</td>
</tr>
<tr>
<td>Asphaltene 1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Residuum 2</td>
<td>42(58)</td>
<td>30(42)</td>
</tr>
<tr>
<td>Asphaltene 2</td>
<td>43(54)</td>
<td>37(46)</td>
</tr>
<tr>
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<td>35</td>
</tr>
<tr>
<td>Asphaltene 3</td>
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<td>50</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Rasa lignite</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>Illinois #6 (APSB)</td>
<td>60</td>
<td>40</td>
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</tbody>
</table>

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Figure 1
S K-edge XANES and 3rd. Derivatives of Petroleums

Figure 2
S K-edge XANES of Coals
IDENTIFICATION OF THE HETEROATOM CONTAINING COMPOUNDS IN THE 
BENZENE/METHANOL EXTRACTS OF THE ARGONNE PREMIUM COAL SAMPLES

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The Argonne Premium Coal Samples (APCS) provide a unique opportunity to study a set of pristine 
samples specifically selected to represent the vast diversity of chemical structures exhibited by U.S. coals. The 
purpose of this paper is to utilize high resolution mass spectrometry (HRMS) to characterize the heteroatom 
containing species that can be extracted from the APCS. Of special interest is the change in structure and 
relative concentrations that these compounds undergo with rank. The resulting information is important in 
providing basic chemical structural information concerning these coals which are being used by a significant 
portion of the coal community, and understanding the transformations that the heteroatom containing species 
undergo during the coalification process.

EXPERIMENTAL

The coals used in this study and their elemental analyses 
are presented in Table I and the preparation of 
the coals has been described in detail by Vorres and Janikowski. The sample handling and extraction procedures 
along with an overview of our overall analysis scheme have been presented previously.

Table I. Elemental analysis of the APCS coal samples used in this study.

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<tr>
<th>APCS Number</th>
<th>Coal</th>
<th>Carbon</th>
<th>Hydrogen</th>
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<td>Beulah-Zap</td>
<td>72.9</td>
<td>4.83</td>
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<td>0.70</td>
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</tr>
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<td>2</td>
<td>Wyodak Anderson</td>
<td>75.0</td>
<td>5.35</td>
<td>1.12</td>
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<td>80.7</td>
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<td>0.37</td>
<td>11.58</td>
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<td>7</td>
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<td>0.65</td>
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<td>0.89</td>
<td>8.83</td>
<td>3.7</td>
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<tr>
<td>1</td>
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<td>4.70</td>
<td>1.15</td>
<td>0.74</td>
<td>7.51</td>
<td>0.5</td>
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<tr>
<td>5</td>
<td>Pocahontas #3</td>
<td>91.0</td>
<td>4.44</td>
<td>1.33</td>
<td>0.50</td>
<td>2.47</td>
<td>1.9</td>
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However, a brief overview the experimental procedure is appropriate here. One hundred grams of the -100 
mesh dried coal was extracted for 48 hours in 250 ml of boiling benzene/methanol azo trope (40/60 w/w 
percent). The extract was removed by vacuum filtration, the residue was washed with 50 ml of the azo trope, 
and dried to constant weight at 100°C under vacuum. The two low rank coals (Wyodak Anderson and 
Beulah Zap) were extracted without drying in order to avoid irreversible physical or chemical changes that are 
known to occur during drying. The azotrope was stripped from the extract at 70°C under vacuum in a rotary 
evaporator and the extract brought to constant weight. The two higher rank coals (Upper Freeport and 
Pocahontas #3) did not yield enough extract for subsequent separation.

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The extract from the six lower rank coals was then separated into nine fractions using the desorption column chromatographic technique (DSEC) developed by Farcasid. The fractions in order include: (1) hexane, (2) hexane/15% benzene, (3) chloroform, (4) chloroform/10% diethyl ether, (5) diethyl ether/3% ethanol, (6) methanol, (7) chloroform/3% ethanol, (8) tetrahydrofuran, (9) pyridine/3% ethanol. In our application of this technique the extract was dissolved in 7 ml of the azeotrope and coated on 6.65 grams of dried silica gel by rotary evaporation of the solvent. The coated silica gel was placed on the top of the column containing 26.8 grams of Aldrich Grade 12 silica gel. This silica gel had been dried for 8 hours at 120°C and then rehydrated to 4 percent water. Blank elutions were performed in order to correct the weight of each fraction for dissolved silica gel.

For the high resolution mass spectra approximately 20 mg of the extract from fractions 3-6 was dissolved in benzene/methanol azeotrope. 0.1 mg of the Diels-Alder adduct of D₆-anthracene and maleic anhydride was added as an internal standard and the resulting solution concentrated to 0.3 ml. The synthesis and applicability of this adduct as an internal standard in HRMS has been discussed previously. The solution was placed on the tip of a glass probe and the solvent was allowed to evaporate. The probe containing the sample was inserted into the all glass inlet system held at room temperature and evacuated. The temperature of the inlet system was rapidly raised to 350°C and the volatilized sample was allowed to leak into the source of the Kratos MS 50 high resolution mass spectrometer. Approximately 10 scans were obtained for each sample at an electron ionization energy of 70 eV, and a scan rate of 100 seconds/decade providing a dynamic resolution of 40,000. The resulting data was transferred to a Micro Vax II for final analysis. This analysis utilized a set of programs developed in house for averaging the scans in the run and assignment of elemental formulae to the averaged masses and sorting by heteroatom content and hydrogen deficiency (HD = rings + double bonds).

RESULTS AND DISCUSSION

The distribution of the extract in each of the DSEC fractions, for each of the coals for which enough extract was available, is shown in Figure 1. Although, no strict correlations are observed, several general conclusions can be drawn. The percentage of the total extract eluting in the hexane (1) and chloroform/10% diethyl ether (4) - Tetrahydrofuran (8) fractions tends to decrease with rank while the hexane/15% benzene (2) and chloroform (3) fractions increase. This is not particularly surprising since we know from elemental analysis that the amount of oxygen decreases with rank while the nitrogen content remains steady or increases only slightly. Yarzab, Given and coworkers have shown that the phenolic content decreases with rank. However, a linear correlation is only observed with carbon content within a single coal provenance. The amount of extract eluting in the hexane (1) fraction shows the tendency to decrease with rank if the Blind Canyon coal is not considered. This coal is unusual in the fact that it exhibits an abnormally high liptinite content. Gas chromatography/mass spectrometry (GC/MS) of this fraction indicates that it is composed almost exclusively of alkanes and cycloalkanes. GC/MS and HRMS of the hexane/15% benzene (2) fraction indicated that only trace amounts of heteroatomic species are present. Thus, the remaining discussion in this paper will be limited to the chloroform (3) through methanol (6) fractions.

The degree of condensation increases with rank for each of the heteroatomic classes of compounds. Figure 2 illustrates this trend using single oxygen containing ions from the chloroform (3) fraction. The two low rank coals (Beulah Zap (#9) and Wyodak Anderson (#3)) are dominated by species with HD values less than 10. An HD of 10 corresponds to an anthracene or phenanthrene type structure if all of the rings are aromatized. A more likely assignment would be a smaller condensed structure with additional aliphatic or partially unsaturated rings. While the higher rank coals exhibit much larger contributions from ions with HD values in the range of 10-19. For the two highest rank coals for which we have data (Pittsburgh (#4) and Lewiston-Stockton (#7)), a maximum in the distribution is observed at HD=12. This corresponds to the empirical formula C₆H₄O for the base structure of the homologous series. This trend was also recognized by Given and coworkers who used catalytic dehydrogenation by Pd/CaCO₃ in boiling phenanthridine.

Oxygen Compounds. Compounds containing one, two and three oxygens are present in the extracts from all of the coals. The distribution of these classes among the fractions are presented in Table 1. Single oxygen containing species are found primarily in the chloroform (3) and chloroform/10% diethyl ether (4) fraction, two oxygen containing species in the chloroform/10% diethyl ether (4) and diethyl ether/3% ethanol (5) fractions, and three oxygen containing species in the methanol (6) fraction. Single oxygen carbonyl compounds of the type...
investigated by Given and Peover may also be present in this fraction. However, their unequivocal identification by HRMS is not possible.

The single oxygen compounds in the chloroform (3) fraction appear to be primarily phenolic in nature with maxima at HD 4, 7, and 10. While those in the chloroform/ether fraction produce a higher concentration of ions at HD = 3, 6, 9 which can be assigned to structures containing five-membered rings or those containing several aliphatic or partially saturated six-member rings. Since compounds of these two types are isomers it is not possible to distinguish between them by HRMS. An example of the HD distribution for these compounds was presented in Figure 2 above.

The two oxygen containing compounds which are found in every fraction are predominantly aliphatic carboxyl based (HD=1) for the low rank coal and dihydroxy or furan based for the coals of higher rank. The carboxyl containing compounds were found in each of the fractions for the lower rank coals but primarily in the methanol fraction (6) for the higher rank coals. The fragmentation pattern of the carboxyl compounds eluting in the less polar fractions indicate that they are most likely esters. These esters which were also observed by Bockrath et al. could be either indigenous to the coal as suggested by Niwa et al. or formed during the extraction in benzene/methanol. This contradicts the work of Miller et al. who claimed that acids were present only lignites, low rank subbituminous and a few Rocky Mountain Hc bituminous coals.

In the low rank coals carboxylic acids are observed with carbon numbers up to 33 while in the higher rank the series ends at 6 carbons.

The three oxygen containing compounds appear primarily at HD = 4, 7, 10 which corresponds to fully aromatized compounds with three OH groups. However, the base compound is not found in the series from any of the coals. This leads to the conclusion that instead of being purely phenolic in nature the three oxygen containing compounds would be very difficult to elute. Somewhat surprising is the amount of aliphatic, and partially unsaturated (HD<4) three oxygen compounds that are found in the methanol fraction. These compounds make up from 17 to 40 percent of all of the three oxygen compounds eluting in this fraction. The difficulty in rationalizing the presence of possible structures for these compounds in coal leads to the possibility that they are either contamination or mis-assignments.

Nitrogen Compounds. Single and double nitrogen containing species eluted primarily in the methanol (6) fraction, but trace amounts of one single nitrogen containing compounds were also observed in the chloroform (3) fraction. In the chloroform (3) fraction three series of alkylated condensed anisoles are present at HD = 6, 9, and 12 for the higher rank coals. Probable structures for these compounds include either the N hybridized C, alkylated forms. Although a definitive conclusion can not be drawn, the discreteness of elution with
two interleaving fractions before the next appearance of compounds exhibiting the same elemental formula, leads to the conclusion that these are the N alkylated forms, as has been proposed previously.

The ratio of HD = 9/10 and 12/13 is plotted versus carbon content in Figure 4. Except for Illinois #6 coal the ratio decreases with rank. The interpretation of this figure is somewhat complicated by the fact that it is impossible to distinguish if the nitrogen is in the 5 membered ring or not. The plot does show that the relative degree of aromaticity increases with rank. Species containing two nitrogen compounds are present in the extract from all of the coals except Beulah Zap. The most prominent series of these compounds is found at HD = 9. A series based on a second compound would have as its base the formula C_{3}H_{4}N_{2} which was not observed. This corresponds to the formula C_{3}H_{5}N_{2} for the base compound.

Sulfur Compounds. All of the extracts contained minor amounts of thiophenic compounds (HD = 6, 9, 12) which eluted in the ether/3% ethanol (5) fraction. Although sulfur is notoriously difficult to identify in HRMS, the small deviations from the expected mass, the generation of rational structures for annulated thiophenes versus irrational structures for alternative classes of compounds, and the observance of the expected HD distribution lead to the conclusion that the assignments are valid. The assignment of sulfur containing structures to possible matches at HD values other than those corresponding to thiophenes would be considerably more tenuous, due to the failure of at least two of the criteria mentioned above.

Mixed Heteroatomic. The mixed heteroatom containing compounds are found primarily in the diethyl ether (5) and methanol (6) fractions. The most prominent species from all of the coals are the hydroxylated pyridines, indoles and their higher order annulates. These compounds follow the same trend (see Figure 5) as that observed for the unhydroxylated indoles and pyridines, showing a decrease in the ratio of the 5 membered ring to that of the 6 membered ring with rank. A significant number of sulfur-nitrogen compounds may also be present in the methanol (6) fraction of the higher rank coals. These compounds are observed primarily at HD = 3, 4, 6, 7, 9, 10, 12, 13. However, as mentioned in the previous paragraph, compounds containing sulfur are notoriously difficult to assign structure due to their small mass defect. Hydroxylated thiophenes were not observed in any of the fractions.

![Figure 2. Variation in HD for single oxygen containing compounds in the chloroform (3) fraction.](image-url)
Table II. Variation of one two and three compounds in DSEC fractions 3-6.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Chloroform (3) One</th>
<th>Chloroform/10% Diethylthe (4) One</th>
<th>Chloroform/10% Diethylthe (4) One</th>
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<tr>
<td></td>
<td>Chloroform/10% Diethylthe (4) One</td>
<td>Chloroform/10% Diethylthe (4) Two</td>
<td>Chloroform/10% Diethylthe (4) Three</td>
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<tr>
<td>Beulah Zap</td>
<td>13.2</td>
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<td>15.3</td>
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<td>18.8</td>
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<td>20.3</td>
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<td>28.3</td>
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<td>33.9</td>
</tr>
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<td>Blind Canyon</td>
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<td>12.2</td>
</tr>
<tr>
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<td>18.1</td>
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<td>50.1</td>
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<td>Lewiston-Stockton</td>
<td>13.9</td>
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<td>30.2</td>
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Diethyl Ether/3% Ethanol (5)

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<th>Coal</th>
<th>Chloroform/10% Diethylthe (4) One</th>
<th>Chloroform/10% Diethylthe (4) Two</th>
<th>Chloroform/10% Diethylthe (4) Three</th>
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</thead>
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<td>Chloroform/10% Diethylthe (4) Two</td>
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<td>Illinois #6</td>
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<td>4.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Blind Canyon</td>
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<td>11.3</td>
<td>2.9</td>
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<td>Pittsburgh</td>
<td>19.2</td>
<td>13.7</td>
<td>7.3</td>
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<td>Lewiston-Stockton</td>
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<td>8.3</td>
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Methanol (6)

<table>
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<tr>
<th>Coal</th>
<th>Chloroform/10% Diethylthe (4) One</th>
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<td>Chloroform/10% Diethylthe (4) Two</td>
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<td>Beulah Zap</td>
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<td>Wyodak-Anderson</td>
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<td>Lewiston-Stockton</td>
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Figure 3. Ratio of HD 9/10 and 12/13 for the single nitrogen containing species in the methanol (6) fraction.
Figure 4. Ratio of HD 9/10 and 12/13 for the oxygen-nitrogen containing compounds in the methanol (6) fraction.

ACKNOWLEDGMENTS

The coal samples were provided by the Argonne Premium Coal Sample Program.

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REFERENCES


ANALYSIS AND COMPARISON OF TWO VICTORIAN BROWN COAL RESINITE SAMPLES

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INTRODUCTION

Amongst the organic constituents of coal, the maceral resinite is probably the least complex structurally, due to the relatively simple composition of the original resins. Hence, with careful analysis, it may be possible to construct meaningful and accurate structural descriptions of this maceral. This is especially true of resinites found in low rank coals, where macroscopic resinite accumulations are relatively common, and in which the effects of catagenetic processes are minimal or absent.

For the purposes of this study, two physically diverse resinite samples were obtained from Victorian Brown Coal (VBC) by hand picking from open cut mine faces. The first sample, which is referred to as "resinite" throughout this text, is a hard, brittle, glassy material, yellow/brown in colour. The second is a soft, brittle, bone white material, which was found in association with a large gymnosperm log, of undetermined paleobotanical affinity, as sheets between "wood" and "bark". This material is sometimes referred to as "bombicite" by geologists, and is referred to by this name in this text in the interests of clarity. Petrographically, both samples are classified as resinite.

EXPERIMENTAL

Pyrolysis-high resolution mass spectra were recorded on a Kratos MS-50 mass spectrometer, operating at a dynamic resolution of 10,000. Ramped pyrolyses (150-800°C, 50°C/min) were used for pyrolysis of these resins in order to minimize thermal reactions in volatile products. Pyrolysates were introduced into the ion source through an all glass heated inlet system, held at 300°C.

FTIR spectra were recorded on a Bruker 113V FTIR spectrometer. Samples were quantitatively prepared as 13 mm KBr discs, and spectra normalized to 1.00 mg (resin) for presentation.

CP/MAS "C NMR spectra were recorded on a Bruker CPX-100 NMR spectrometer, operating at a field strength of 2.35 T. Relevant operating parameters were as follows: spectral width = 10 kHz, contact time = 2 ms, pulse repetition rate = 2 sec, proton decoupling field = 56 kHz. Interrupted decoupling experiments used a 100 μs interruption to proton decoupling prior to acquisition.

RESULTS AND DISCUSSION

The results of pyrolysis-high resolution mass spectrometric analysis (Py-HRMS) of the resinite and bombicite samples characterized during the course of this study are illustrated in Figure 1. The close similarity of these data suggests that despite their physical dissimilarity, the chemical structures of these materials are very similar. In particular, these data indicate that species of molecular weight = 302, molecular formula = C₉₃H₁₆₂O₃ are a predominant subunit in both materials. This suggests that the macromolecular structures of these materials are based predominantly on diterpenoid monomers.

The results of spectroscopic analyses of resinite and bombicite are illustrated in Figures 2 (CP/MAS "C NMR) and 3 (FTIR). The combination of normal CP/MAS "C NMR, CP/MAS "C NMR with interrupted proton decoupling (which reduces or eliminates signal due to protonated carbon) and FTIR, allows considerable
structural detail to be elucidated. Both $^{13}$C NMR and FTIR data suggest that both the resinite and bombicite have predominantly aliphatic structures (which is consistent with the elemental composition of these samples - see Table 1). Also indicated is the presence of considerable amounts of oxygen containing functional groups, especially carboxylic acids. The absence of appreciable intensity in the 30 ppm region of the $^{13}$C NMR spectra of these samples, and the lack of characteristic dominant IR absorption bands at 2926 cm$^{-1}$ and 2853 cm$^{-1}$ in the corresponding FTIR spectra, rule out the presence of polymethylene structures of significant chain length. Rather, the spectroscopic data suggest that their structures are based to a large extent on alicyclic structures. Strong IR absorptions at 1450 cm$^{-1}$ and 1385 cm$^{-1}$ in the FTIR spectra of both samples suggest a high degree of methyl substitution. Moreover, the partial disappearance of carbon resonances, at 15 ppm, 20 ppm, and 29 ppm in the proton decoupling interrupted $^{13}$C NMR spectra, suggests that methyl groups exist in these samples in at least three structurally distinct environments.

$^{13}$C NMR resonances at 108 and 149 ppm, and moderately intense IR absorption at 887 cm$^{-1}$ indicate the presence of exocyclic R,C=CH$_2$ structures. Similarly, $^{13}$C NMR resonances at 126 ppm and 139 ppm, which are absent and present respectively in the interrupted decoupling spectra, indicate that significant amounts of 1,1,2-trisubstituted C=C bonds are present in both samples. Significant carbonyl functionality in these materials is established by $^{13}$C resonances at 180-190 ppm and strong FTIR absorbance at 1695 cm$^{-1}$.

Other types of oxygen containing structures are also indicated by the spectroscopic data, although these differ between samples. The $^{13}$C NMR resonance observed at 203 ppm (absent in the interrupted decoupling spectra) and IR absorbance at 1720 cm$^{-1}$ in the spectra of the resinite sample, indicate that aldehydic compounds may contribute significantly to the structure of this material, and $^{13}$C resonance at 72 ppm in the spectra of the bombicite sample indicates the incorporation of alcoholic or etheric structures into this material.

The results of analysis therefore suggest that these materials are based on cyclic diterpenoid units, which incorporate a significant degree of methyl substitution. The presence of an exocyclic C=C bond, and another, 1,1,2-trisubstituted C=C bond is also indicated, as is the presence of carbonyl functionality. The inclusion of compounds of other structural composition, especially with respect to the nature of oxygen containing functional groups, is also indicated, but the structural units having the features described above appear to predominate, and are common to both samples.

It has been noted that macroscopic resinite accumulations in VBC often occur in association with fossil logs of the genus Agathis. This association has not been specifically established for the samples used in this study, except, as already noted, that the bombicite sample characterized was found in intimate association with a large gymnosperm log. Nevertheless, this relationship has been established for a significant number of closely similar samples, and it is highly probable that the samples used in this study are derived from the bled resins of this species.

Modern Agathis resins were at one time of considerable commercial value, and as such, have been the subject of numerous investigations. Analysis of fresh bled resins of this species have demonstrated that the major components present are diterpenoid acids, specifically, those with the structures illustrated in Scheme 1. It has also been established that the solvent extracts of VBC resinites are rich in these acids, especially agathic acid, and their degradation products. Based largely on the foregoing work, and more recently on spectroscopic evidence, previous workers have proposed structures for these resinites based on poly-agathic acid. The mechanism proposed by these workers suggests that these resinites are formed by polymerization of (mainly) agathic acid with loss of the terminal C-15 carboxyl group. Such a polymeric structure would therefore be based predominantly on C$_n$ monomers. The results of the analyses reported here however, clearly demonstrate the predominance of C$_n$ products in both VBC resinite and bombicite, and hence preclude C$_n$ monomers as a major structural subunit in these samples. The structure proposed by these authors, however, very closely resembles those which can be drawn for the polymerization products of cis- and trans-communic acids, (as illustrated in Scheme 2), which are major components of fresh Agathis resins. These acids are known to readily polymerize on exposure to the atmosphere, and in some cases, poly-Communic acids have been shown to constitute a significant fraction of fresh and recent resins.
Scheme 1.

Scheme 2.
CONCLUSIONS

The results of this study of VBC resinites suggest that these materials are not based on poly-agathic acid structures as has been previously proposed. The data obtained indicate the predominance of structural subunits of molecular formula $C_{m}H_{n}O_{s}$, which are consistent with a poly-communic acid based polymeric resinite structure. Other materials may be incorporated into the polymeric structure to a lesser degree, and may also be physically occluded within it.

ACKNOWLEDGMENTS

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38. The authors would like to thank Dr. T.V. Verheyen, Coal Corp. of Victoria, for supplying the samples used in this study.

REFERENCES


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<th>TABLE 1.</th>
<th>Elemental Composition (wt%)</th>
<th>Molecular Formula (based on C$_m$)</th>
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<tr>
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</tr>
<tr>
<td>poly-Communic Acid</td>
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<td>9.9</td>
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Figure 1. Mass spectra of selected ion classes obtained by Py-HRMS of VBC resinite and bombicite (averaged over 50 scans).
Figure 2. CP/MAS $^{13}$C NMR spectra, and Interrupted Proton Decoupling (I.Dc.) CP/MAS $^{13}$C NMR spectra of VBC resinite and bombicite.
Figure 3. FTIR spectra of VBC resinite and bombicite.
SWELLING OF COAL EXTRACTS

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Western Kentucky University
Bowling Green, KY 42101

INTRODUCTION

Coals are considered macromolecular solids. (1) Although they are not polymers in the sense that they possess a repeating unit, they do possess several fundamental properties typical of synthetic crosslinked polymers. (2) One of these properties is the ability of coals to swell in organic solvents without dissolving.

In recent years, there has been a rapid growth in the number of publications that deal with the solvent swelling of coal. Much of this effort has been directed toward the application of modern polymer and network theories to coal, with the purpose of better understanding their network structures. One of the most fundamental properties of a network structure is \(M_g\), the average molecular weight between crosslinks. Consequently, several research groups have attempted to estimate \(M_g\)'s for coal from solvent swelling data and the Flory-Rehner equation. (3-8) The equation incorporates both the Flory-Huggins theory of polymer solutions and the Gaussian elastic network theory. An important parameter embodied in the Flory-Huggins theory is the interaction parameter, \(\chi\). \(\chi\) is a thermodynamic parameter describing the energetics of the polymer-solvent interaction. A reliable evaluation of \(\chi\) is essential for an estimation of \(M_g\) for crosslinked networks using the Flory-Rehner equation. Very few reliable methods have been developed to evaluate \(\chi\) for coal-solvent systems. It is the purpose of this research to develop a reliable method for its evaluation.

Approach. One of the most common techniques for determining \(\chi\) parameters for polymer-solvent systems is the vapor sorption method. (9) In this approach, the uncrosslinked polymer is exposed to solvent vapor of known pressure, \(p\). The polymer absorbs solvent until equilibrium is established. \(\chi\) is related to \(p\) and \(v_2\), the volume fraction of polymer at equilibrium, by

\[
\chi = \frac{\ln \left( \frac{(p/p_o)^2}{(1-v_2)} \right)}{v_2^2} - v_2
\]

Measurement of \(p\) as a function of \(v_2\) can be used with Equation 1 to obtain values for \(\chi\) over a wide range of concentrations.

It is important to recognize that Equation 1 applies to polymers that are not crosslinked. Most vapor sorption studies on coal have been conducted on the crosslinked, or insoluble portion of coals. Under this condition, simultaneous evaluation of \(\chi\) and \(M_g\) must be made. Two groups of researchers have adopted this approach. (7,8) We have adopted an alternative approach by conducting vapor sorption studies on the uncrosslinked portion of the coal. \(\chi\) parameters can thus be directly calculated from the pressure-sorption data using Equation 1.

The uncrosslinked portion of the coal is obtained by Soxhlet-extraction of the coal with pyridine. Pyridine is a particularly good solvent for coals, and it is thought to remove a majority of the uncrosslinked molecules from the coal matrix. There is evidence that the pyridine-soluble portion is representative of the larger, crosslinked portion, although this aspect remains controversial.
EXPERIMENTAL

Sample Preparation. Dry Illinois No. 6 (Herrin seam, -60 mesh) was used in the sorption studies. Analysis Found: C, 74.37; H, 4.83; N, 1.76; S, 1.76; O (by difference), 8.74; Ash, 8.33 (duplicate). Approximately 10 g of the sample was exhaustively Soxhlet-extracted with pyridine. Extractability was 18.7% (wt.). The pyridine solution was then filtered through a 0.4 μm filter. Most of the pyridine was removed by rotovaporization under reduced pressure at 70-80°C. Approximately 200 mL of a methanol/water (80/20 vol) mixture and 2 mL of conc. HCl were added to the flask and the mixture was stirred under nitrogen for two days. The solid extract was then filtered and dried under vacuum at 115°C for 24 hours.

Analysis Found: C, 82.97; H, 5.87; N, 1.80 (duplicate).

O-Methylation Procedure. The extract was O-methylated according to a method described earlier by Liotta (10) using tetrabutylammonium hydroxide and methyl iodide.

Sorption Experiments. Sorption experiments were carried out using a Cahn 1000 recording balance, with an accuracy of ±0.03 mg. The balance and its accessories are shown in Figure 1. The instrument is equipped with an MKS Baratron pressure transducer (0-100 torr, 0.15% accuracy) with a digital readout for pressure measurements.

Prior to conducting the sorption experiment, the coal extract (200 mg) was first placed in a Wig-L-Bug capsule and ground for 1 minute under nitrogen. This grinding effectively reduces the extract to a fine powder, which is then used for the sorption experiment. Approximately 50-70 mg of the extract was then placed on the sample pan and the hangdown tube was replaced. The sample was maintained at 30.00 ±0.02°C by means of a constant temperature bath which surrounded the hangdown tube.

In a typical experiment, benzene vapor was admitted into the evacuated balance chamber by means of stopcock D. After achieving the desired pressure, stopcock D was closed. The maximum uncertainty in p/p0 during the course of any one experiment was ±0.008 units. Equilibrium was judged to be established when there was less than a 1 percent change in weight over a 12 hour period.

RESULTS

Characterization of the Pyridine-Extract. Pyridine is known to cling to coals. The extract was therefore stirred with a methanol/water/HCl mixture for two days as suggested by Buchanan.(11) Elemental analysis of the extract revealed 1.80% N. The original coal contained 1.92% N (daf) so it is apparent that the methanol/water/HCl treatment followed by drying successfully removed pyridine from the extract.

Synthesis and Characterization of O-Methylated Extract. The O-alkylation of coals has been discussed by Liotta et al.(10) Alkylation occurs when tetrabutylammonium hydroxide is used to promote the reaction of the alkyl iodide with the coal in tetrahydrofuran. The alkylation reaction occurs primarily on acidic oxygen functionalities such as phenolic hydroxyl and carboxylic acid groups, as shown below.

\[
\text{Coal-OH} + \text{R}_n\text{N}^+\text{I}^- \rightarrow \text{Coal-OR} + \text{R}_n\text{N}^+\text{OH}^- + \text{H}_2\text{O}
\]
The hydrogen to carbon ratios of the extract and O-alkylated extract established that 4 hydroxyl groups per 100 carbon atoms were alkylated. FT-IR and $^{13}$C NMR analysis confirmed that O-methylation had occurred.

**Sorption Experiments.** The extracts were exposed to benzene vapor at several relative vapor pressures ($p/p_0$). Two types of sorption experiments were conducted. Experiments in which the benzene vapor pressure is raised from zero to a higher value are termed *integral* sorptions. Sorption experiments starting with the extract and vapor in equilibrium at a finite, non-zero pressure, and proceeding to a higher pressure, are termed *incremental* sorptions.

Figures 2 and 3 show the sorption curves of mass uptake versus time for the extract and O-methylated extract. Three different experiments are shown in each figure; a single integral sorption and two subsequent incremental sorptions. Both extracts required 30 to 150 hours to reach equilibrium, depending on the particular experiment.

**Sorption-Desorption Isotherms.** Sorption-desorption isotherms for the extracts are presented in Figures 4 and 5, where the relative vapor pressure of benzene ($p/p_0$) is plotted against the cumulative equilibrium uptake of benzene. Both isotherms are characterized by strong hysteresis (non-reversible sorption behavior). For both extracts, a considerable amount of benzene cannot be desorbed under vacuum (~0.01 torr). However, the benzene could be completely removed from the O-methylated extract by heating to 105°C under vacuum. Thus benzene is not irreversibly bound to the O-methylated extract. Once the benzene was driven off, the sorption curve could be reproduced. We did not apply this procedure to the extract, but we expect it to behave similarly.

**DISCUSSION**

The sorption of benzene by the extract and the O-methylated extract is characterized by a rapid, initial uptake followed by a slow approach to equilibrium. Such sorption behavior is very similar to that of glassy polymers. Thus we have chosen to interpret the sorption curves shown in Figures 2 and 3 in terms of the Berens-Hopfenberg model developed for sorption of organic vapors into glassy polymers.(12)

The Berens-Hopfenberg Model. The Berens and Hopfenberg model considers the sorption process in glassy polymers as a linear superposition of independent contributions of a rapid Fickian diffusion into pre-existing holes or vacancies (adsorption) and a slower relaxation of the polymeric network (swelling). The total amount of sorption per unit weight of polymer may be expressed as

$$M_L = M_{L,F} + M_{L,R}$$

where $M_{L,F}$ and $M_{L,R}$ are the contributions of the Fickian and relaxation processes, respectively.

The relaxation or swelling process is assumed to be first order in the concentration difference which drives the relaxation and is expressed as

$$M_{L,R} = M_{L,R} [1 - \exp (-kt)]$$

where $k$ is the relaxation rate constant and $M_{L,R}$ is the ultimate amount of sorption due to relaxation. The relaxation process is interpreted as a structural reordering.
or swelling of the polymeric network. It is the swelling term which is of crucial importance to our study.

**Interpretation of Sorption Curves.** The slow asymptotic approach to equilibrium exhibited by the extract and O-methylated extract, as shown in Figures 2 and 3, strongly suggest that this process might correspond to the first-order relaxation or swelling process described in the Berens-Hopfenberg model, and that the initial rapid uptake may correspond to hole filling and/or adsorption onto surfaces. To test whether this slow process follows first-order behavior, we have plotted the natural log of the difference between the equilibrium sorption value, $M_e$, and the sorption value at any time, $M_t$, against time. The results are shown in Figures 6 and 7. Note that a substantial portion of each curve is linear or nearly linear at long times, indicating a first-order process. This is particularly evident for the incremental sorption where linearity is observed over a 50 to 60 hour period. At short times, the curves clearly deviate from linearity, suggesting that other processes are dominating.

We suggest that the rapid process corresponds to hole-filling and/or adsorption onto external surfaces, and that the slow process, which follows first-order behavior, corresponds to swelling of the coal extract. Extrapolation of the linear portion of the curves shown in Figures 6 and 7 to time zero should yield the total uptake of benzene attributed to swelling. The results of this analysis are summarized in Table I, where the total benzene uptake, $M_e$, and the uptake attributed to the hole-filling/adsorption and the swelling processes, $M_{ads}$ and $M_{swell}$, are shown.

If this interpretation of the sorption process is correct, it indicates that when the benzene pressure is raised from zero to an activity of 0.22, the dominant process is hole-filling and/or adsorption, with only a relatively minor contribution from actual swelling. However, in subsequent incremental sorptions, the swelling process is clearly dominant. These results are similar to those of Berens and Hopfenberg in their studies on glassy polyvinylchloride.(12) According to their interpretation, the polymer is initially penetrant-free in an integral sorption experiment, and the hole-filling process therefore dominates. Incremental sorptions, however, proceed with polymer in which most of the sorption holes are pre-saturated. The relative contribution of swelling is therefore larger in these experiments.

The data in Table I also indicate that the O-methylated extract swells roughly one and a half times the extract. These results are consistent with those of Larsen et al.(6), who observed that O-methylated coals swell substantially more than underivatized coals.

The swelling data in Table I can be used to calculate $\chi$ parameters for the extract and O-methylated extract using Equation (1). A knowledge of the densities of the extracts is required to convert the masses to volume fractions. We have assumed densities of 1.4 and 1.3 g/mL for the extract and O-methylated extract, respectively. These are the helium densities (dmmf basis) for the Illinois No. 6 coal and its O-methylated derivative as determined by Liotta.(10) A density of 0.88 g/mL for benzene was used. Additivity of volumes was also assumed. The results of these calculations are shown in Table II.

The $\chi$ parameters are observed to be positive and independent of vapor pressure (or concentration). According to Flory-Huggins theory, polymer-solvent systems with $\chi$ parameters above 0.5 should show only limited solubility.(2) Thus the extracts
should not dissolve in liquid benzene but should show limited swelling. Liquid volumetric swelling measurements verify this expectation. The bulk of both extracts remain insoluble in liquid benzene, although some dissolution occurs. Moreover, both extracts exhibit limiting swelling, with the 0-methylated extract swelling more than the extract, consistent with the gravimetric data presented in Table I. χ parameters were calculated from the volumetric data assuming a p/p₀ of 1.0, and are shown in Table II. The volumetric method yields χ parameters consistent with those calculated from the gravimetric data.

Finally, a calculation of the solubility parameter of the extracts can be made using the equation

$$\delta_e = \left(\frac{\chi - 0.30RT}{V}\right)^\frac{1}{2} + \delta_s$$

where \(\delta_e\) and \(\delta_s\) are the solubility parameters of the extract and solvent, respectively, and \(V\) is the molar volume of benzene (89 mL/mol). Using a \(\delta_s\) of 9.2 Hildebrands for benzene and a \(\chi\) of 1.5 for the extract, \(\delta_e\) of 12.0 Hildebrands is calculated for the extract. The same calculation using a \(\chi\) of 1.1 for the 0-methylated extract yields a \(\delta_e\) of 11.5 Hildebrands. Van Krevelen has estimated solubility parameters of coals using a group contribution method and has calculated values ranging from 10.6 to 15.2 Hildebrands. Thus the solubility parameters calculated for the extracts fall within the accepted range of solubility parameters for coals.

CONCLUSIONS

The sorption of benzene by an extract and 0-methylated extract of an Illinois No. 6 coal is characterized by an initial, rapid uptake of solvent vapor, followed by a slow asymptotic approach to equilibrium. The slow process appears to follow first-order behavior. We have suggested that this slow, first-order process corresponds to the swelling of the extract. There are several lines of indirect evidence to suggest that this interpretation is correct.

(1) The results show that the 0-methylated extract swells more than the underivatized extract, consistent with other swelling studies.

(2) The χ parameters calculated for the benzene-extract systems are consistent with the fact that the bulk of these extracts remain insoluble in liquid benzene. The extracts, however, exhibit limited swelling. The χ parameters calculated from the volumetric data are consistent with those derived from the gravimetric data.

(3) The solubility parameters of the extracts calculated from the χ parameters fall within the accepted range of solubility parameters for coals.

ACKNOWLEDGEMENT

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REFERENCES


TABLE I

<table>
<thead>
<tr>
<th>Pressure Interval ( p/p_0 )</th>
<th>Extract (mg/g)</th>
<th>0-Methylated (mg/g)</th>
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<tr>
<td>0 - 0.22</td>
<td>76 64 12</td>
<td>78 56 22</td>
</tr>
<tr>
<td>0.22 - 0.44</td>
<td>38 17 21</td>
<td>32 7 25</td>
</tr>
<tr>
<td>0.44 - 0.66</td>
<td>34 12 22</td>
<td>50* 6 44</td>
</tr>
</tbody>
</table>

Total: 148 93 55 160 69 91

* \( p/p_0 = 0.44 - 0.67 \)
TABLE II

Volume Fractions of Solvent and $\chi$ Parameters for the Extract and O-Methylated Extract of Illinois No. 6 Coal and Benzene

<table>
<thead>
<tr>
<th>$P/P_0$</th>
<th>$\chi_1$</th>
<th>$\chi$</th>
<th>$\chi_1$</th>
<th>$\chi$</th>
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</thead>
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<tr>
<td>0.22</td>
<td>0.019</td>
<td>1.5</td>
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</tr>
<tr>
<td>0.44</td>
<td>0.050</td>
<td>1.4</td>
<td>0.065</td>
<td>1.1</td>
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<tr>
<td>0.66</td>
<td>0.080</td>
<td>1.4</td>
<td>0.12</td>
<td>1.1*</td>
</tr>
<tr>
<td>1.0b</td>
<td>0.12</td>
<td>1.6</td>
<td>0.25</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* $P/P_0 = 0.67$

b $\chi_1$ determined from direct volumetric swelling method using liquid benzene.

Figure 1. Sorption Apparatus
Figure 2. Sorption of Benzene by the Pyridine-Extract of Illinois No. 6 Coal at 30°C.

Figure 3. Sorption of Benzene by the O-methylated Extract of Illinois No. 6 Coal at 30°C.
Figure 4. Sorption-desorption Isotherm for the Extract of Illinois No. 6 Coal and Benzene at 30°C.

Figure 5. Sorption-desorption Isotherm for the O-methylated Extract of Illinois No. 6 Coal and Benzene at 30°C.
Figure 6. Plot of $\ln(M_a-M_T)$ versus Time for Extract-Benzene System.

Figure 7. Plot of $\ln(M_{oa}-M_T)$ versus Time for O-methylated Extract-Benzene System.
SPECTROSCOPIC STUDIES OF COAL PYRIDINE EXTRACTS

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This study is part of a larger program aimed at developing an FTIR methodology for the quantitative determination of the aliphatic and aromatic CH content of coals. Although a number of infrared studies of these quantities have appeared, there remains significant differences in the values reported by different groups, reviewed in reference 1. A recent publication by Solomon and Carangelo (2) is not included in this review and is a significant addition to the literature. The origin of these discrepancies is largely due to the difficulty in determining adsorptivities or absorption coefficients, those quantities that relate the intensity of an infrared band to the concentration of functional groups giving rise to that particular absorption. There are essentially three ways of doing this:

a) calibrate using model compounds;
b) equate the hydrogen content (from elemental analysis) to the sum of the functional group contributions;
c) calibrate using soluble coal extracts.

The first is obviously unsatisfactory, not least because it begs the question "what is the structure of coal and hence what is an appropriate model compound." The second method was pioneered, in its application to FTIR studies, by Peter Solomon and his group (2-5), but is equivalent to a procedure described by von Tschamler and deRuiter more than 25 years ago (6). The hydrogen content of the coal is equated to the sum of the contributions from various functional groups

\[ H_T = H_{OH} + H_{ar} + H_{al} \]

where the total hydrogen content \( H_T \) is measured by elemental analysis and \( H_{OH} \) is determined by FTIR or other measurements. [COOH groups should also be measured in low rank coals]. Then;

\[ [H_T - H_{OH}] = E_{ar}I_{ar} + E_{al}I_{al} \]

where \( E_{ar} \) and \( E_{al} \) are "conversion factors" (an inverse function of the absorption coefficients) and \( I_{ar} \) and \( I_{al} \) are the intensities of appropriate infrared bands. If a set of coals of roughly the same character (rank) are studied, we can assume \( E_{ar} \) and \( E_{al} \) are constants for that set and, from the experimentally measured values of \( H_T, H_{OH}, I_{ar} \) and \( I_{al} \), solve as a set of simultaneous equations for \( E_{ar} \) and \( E_{al} \). As we have found in previous studies, however, this set of simultaneous equations is classically ill-conditioned (reviewed in detail in reference 1). In other words, even small experimental errors in a limited sample set results in the calculation of a range of almost equally valid solutions. In their recent study Solomon and Carangelo (2) employ the same method, seeking to improve the accuracy of their calculations by including data from coal chars, and conclude that there is also a variation in absorption coefficients with rank. They are no doubt right, but the problems with this methodology have not been overcome. Furthermore, in forming chars certain types of alkyl groups are preferentially cleaved and lost as volatiles while the remainder of the coal molecule undergoes a degree of reorganization that depends upon the conditions of char formation. This could also lead to some variation in absorption coefficients.

The final method listed relies on the fact that the aromatic and aliphatic CH content of soluble material can be directly determined by proton nmr, thus allowing the absorption coefficients of infrared

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bands of the same sample to be unambiguously calibrated. Of course, if the extract is significantly
different in structure to the parent coal, thus having different absorption coefficients, these values would
not be transferable. This is indeed the case for those coals where there is a high proportion of
extractable long chain alkanes. Fortunately, the CH stretching vibrations of paraffin-like materials are
characteristically sharp and readily recognizable and the correspondence in the spectra of most extracts
and their parent coals demonstrates a similarity in structure. Clearly, in order to determine the range of
absorption coefficients associated with coal structure of varying degrees of aliphatic character by this
method it is necessary that we obtain and study a wide range of samples. This serves to define the range
of inevitable experimental error.

Accordingly, at this point we see no substitute for a slow, meticulous, brute-force approach to data
collection and analysis. During the past 3 years we have obtained the pyridine extracts of more than
thirty-five U.S. coals and seventeen Polish coals. In this brief communication space does not permit a
full description of the characteristics of these samples and the details of our analytical procedures; these
will be presented elsewhere, but the FTIR methodology is similar to that described previously (1). Here
we will simply present an overview of our results.

The data from proton nmr studies of the coal extracts, together with elemental analysis and a
knowledge of the OH content (from FTIR studies of acetylated samples), allows the aromatic and
aliphatic hydrogen contents of the coals to be determined. Preliminary results are shown in figure 1.
Although there is some scatter, to be expected from materials as heterogeneous as coal, the data is fairly
closely grouped and clearly shows the expected trend of decreasing aliphatic CH content and increasing
aromatic CH content with rank (% carbon content of parent coal).

In principle, this data can now be applied to a determination of the absorption coefficients of
infrared bands assigned to aromatic and aliphatic CH groups. In practice, errors play a major role in
determining the accuracy of this procedure. Figure 2 shows a plot of the ratio of the intensities of the
aromatic and aliphatic CH stretching modes, determined as band areas (from samples prepared as KBr
pellets) by curve-resolving procedures described elsewhere (1). There is some scatter in the results that
is not simply a matter of the natural variability of aromatic and aliphatic CH content in coals from
different sources. Obviously, a plot of the ratio of the intensities of the infrared bands should follow the
ratio determined by proton nmr. This relationship need not be linear, if absorption coefficients vary
with rank, but should at least be systematic Figure 3 shows that although a consistent trend can be
obtained and a reasonable average value of the ratio of absorptivities determined, the effect of cumulative
errors in the data is such that it is not possible to determine any variation with rank with any degree of
certainty. The precision in this data can only be improved by averaging the results of additional
spectroscopic analysis of these samples, a time consuming process which we are presently in the
process of performing.

Finally, we are also analyzing the same samples by diffuse reflectance measurements, so that the
two FTIR methodologies can be directly compared. A plot of the ratio of intensities of the aromatic to
aliphatic CH stretching modes against the ratio of the aromatic to aliphatic CH content determined by
proton nmr is shown in Figure 4. The ratio of the values of the absorption coefficients is somewhat
different to that determined from KBr pellets, but again errors, particularly in some of the high rank
(larger H-aromatic/\(H_{aliphatic}\) ratio) coals necessitates additional work. Again a reasonable average value can be
determined, but the subtleties of variation with rank are beyond detection given the present precision of
the data.

Acknowledgement

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Chemical Sciences, Department of Energy, under Grant No. DE-FG02-86ER13537.
References


Figure 1. Plot of the aliphatic and aromatic hydrogen content of a set of U.S. and Polish (PL coals), determined by proton nmr.

Figure 2. Plot of the ratio of the infrared band areas of the aromatic and aliphatic CH stretching modes for the set of extracts.
Figure 3. Plot of the ratio of the band areas of the aromatic and aliphatic infrared stretching modes vs the ratio H_ar/H_at determined by proton nmr.

Figure 4. Plot of the ratio of the aliphatic to aromatic CH stretching modes determined by DRIFT to the ratio H_ar/H_at determined by proton nmr.
LASER ABLATION FOURIER TRANSFORM MASS SPECTROMETRIC INVESTIGATION OF COALS AND RELATED MODEL SUBSTANCES

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INTRODUCTION

Laser ablation Fourier transform mass spectrometry (LA/FTMS) is a technique which allows the investigation of high molecular weight involatile materials. Coals and cokes represent a class of such materials and in general, mass spectrometric analyses of such carbonaceous materials have generally been restricted to thermal desorption gas chromatography-mass spectrometry. Batts and Batts [1] have recently reviewed the application of mass spectrometry to coal analysis.

The use of pulsed high power lasers in mass spectrometry as a soft ionization technique is now well established and has facilitated the investigation of macromolecular species of several thousand mass units [2]. The pulsed nature of the Fourier transform mass spectrometer and high powered pulsed IR or UV lasers represents a logical combination for laser ablation experiments. This technique offers several advantages [2-4], the most important of which are high mass resolution and extended mass range, over other mass spectrometric methods which incorporate time-of-flight or deflection type analysers and other 'soft ionization' techniques.

The carbon content of coal directly reflects its rank and level of maturity. During coalification, the terrestrial organic matter is modified by geochemical processes to ultimately form anthracitic coals. Particularly significant is the transition observed at about 89% carbon content where aromatic lamellae in the coal begin to condense to form polycyclic aromatic compounds. These polynuclear species are important components of anthracitic coals where they form the basis for the further growth of graphite sheets.

In this study, we have examined by FTMS different rank coals and model systems. The latter include graphite and different ring size polynuclear aromatic hydrocarbons. The ionization mechanisms and the effects of irradiances conditions have also been examined.

EXPERIMENTAL

Table 1 presents the maceral compositions and elemental analyses data for the coal samples studied. These included two American anthracitic coals; obtained from the Pennsylvania State University sample bank, and an Australian semi-anthracitic coal and lignite. The graphite and individual polynuclear aromatic compounds were obtained from commercial sources, and were of such purity to be used as received.

The mass spectra were obtained using a Bruker CMS-47 FT/ICR mass spectrometer equipped with a 4.7T superconducting magnet and a 24 bit/256 K Bruker ASPECT 3000 computer. The stainless steel high vacuum chamber and direct insertion probe were evacuated by Balzers 330 lsec⁻¹ and 50 lsec⁻¹ turbo molecular pumps, respectively. For the laser ablation experiments, the samples were finely powdered together with NaCl and pressed into a detachable cylindrical stainless steel satellite probe tip. This in turn was inserted, using a Bruker direct insertion probe, into a titanium single section cylindrical (r=30 mm, h=60 mm) ICR cell.
A typical laser ablation experiment involved focusing the laser beam (1064 nm, Spectra Physics DCR-11) of a Nd-YAG laser to 0.1 mm at the sample satellite probe tip. The sample surface was subjected to laser beam irradiances in the range of 0.005-1000 MWcm⁻², with reproducible irradiance variations being obtained by using neutral density filters. Two laser irradiance times were used in the experiments, corresponding to a long pulse mode (230 µs) and a Q-switched mode (8 nsec). Through careful regulation of the laser irradiance near the ionization threshold it was possible to monitor the effect of laser irradiance on the resulting mass spectra. A normal pulse sequence consisted of the laser irradiation followed by a 1 second delay, prior to data acquisition to allow the desorbed neutral species to be evacuated and the pressure to return to 1×10⁻⁸ mbar. Ions were trapped in the cell by potentials of approximately 4V. The transient was stored as 64 k data points prior to Fourier transformation to obtain a magnitude mode spectrum. For the results reported here, no attempt was made to improve resolution of the high mass carbon clusters by selecting smaller mass ranges, to improve the density of data points.

RESULTS AND DISCUSSION

Model Systems

Figure 1 shows the mass spectra of two of the polynuclear aromatic hydrocarbon compounds; chrysene and fluoranthene. The most abundant ions in each spectra result from the molecular ion, M⁺, and the adduct ion [M + X]⁺, where X is Na⁺. This ion distribution was found for all the polynuclear aromatic model compounds, for the laser ablation experiments. This result indicates the occurrence of at least two different ionization pathways. The presence of adduct ions in the mass spectra indicates a surface laser desorption mechanism, with attachment of alkali metal ions to involatile molecules [5]. For example, in Figure 1(a) the adduction of chrysene, [C₁₈H₁₂Na⁺]⁺ (m/z 251) results from the attachment of Na⁺ to the aromatic compound to form the ionized species, with subsequent volatilization by laser desorption.

In contrast, there is no information to allow a confident prediction of the M⁺ molecular ion formation mechanism. It could be a laser desorption process, where simultaneous ionization and vaporization of the condensed phase leads to the formation of the M⁺ ions. Alternatively, a multiphoton ionization mechanism, where neutrals, which are desorbed by the initial part of the laser pulse, are ionised by photons in the latter part of the laser pulse may be occurring. Yet another possibility is ion/molecule reactions, where smaller desorbed species recombine in the emitted plasma cloud. However, the important point to note is that there is more than one ion formation mechanism possible [6] and it is unlikely in any high power laser ablation experiment that all ions are formed by a single ionization process. Considering the uncertainty concerning these ionization mechanisms for M⁺ formation, it appears that laser desorption ionization of involatile surface species may only be unequivocally assigned from adduct ions.

Interestingly, laser ablation of the graphite sample (Figure 2(a)) at similar irradiation conditions as the model compounds gave only M⁺ spectra. The mass distribution observed for the carbon cluster ions ranged from C₁₁⁺ to C₂₈⁺, with the most intense ions at C₁₅⁺ and C₁₉⁺. Laser ablation FTMS studies on graphite have been previously reported by McElvany et al. [7], who observed carbon clusters up to C₁₈₀⁺, with the most stable species being C₆₀⁺. Compared with the present study, this earlier investigation used (1) a different instrument configuration, (2) different irradiation conditions, and (3) ejected all species below C₁₈⁺ to enhance the resolution of the higher molecular weight carbon clusters. It has also recently been reported that C₆₀⁺ is remarkably stable and is, in fact, a spherical aromatic molecule with a truncated icosahedron (soccer ball) structure. Indeed, carbon clusters have been proposed as being important as nucleation agents for soot formation and being present in interstellar dust clouds [8].
The absence of \([M + Na]^+\) adduct ions in the mass spectrum means that it is difficult to determine, unequivocally, whether the carbon cluster ions are formed from surface species by simple volatilization and photodissociation (i.e. a laser desorption process) or are formed in the gas phase by the other ionization mechanisms, the latter of these being more likely [7]. It is also possible in laser desorption experiments that the adduct ions are not observed, as very large aromatic species may not necessarily form stable adducts with Na⁺.

Negative ion carbon clusters have also been observed for the graphite sample (Figure 2(b)), with the largest cluster being at C_{25} (m/z 300). The detection of negative ions is easily performed in the FTMS by reversing the polarity of the trapping plate potentials. The negative ion carbon cluster distribution does not resemble that of the cations. Only smaller carbon cluster anions are stable. The difference between the anion and cation clusters can be attributed to a different mechanism of formation. The emitted plasma cloud is made up of ions, neutrals and electrons, and electron attachment is believed to be the mechanism of formation for the anionic clusters. It is reported that these carbon cluster anions do not undergo reaction with neutral carbon species in the plasma to form larger carbon clusters (>C_{30}) [7].

**Coals**

Laser ablation of all the anthracitic coals only generated charged carbon clusters. There was no evidence of adduct ion formation in the mass spectra, even when the samples were heavily doped (i.e. 20:1) with alkali metal salts. Figure 3(a&b) shows the mass distributions for the cationic \(C_n^+\) where \(3n \leq 150\) and anionic \(C_n^-\) where \(2n \leq 425\) carbon clusters from the Australian anthracitic coal. The mass distributions are typical of those also observed for the two American anthracitic coals. In all cases, the most intense and stable cationic carbon cluster was \(C_{60}^+\), and the mass distributions were similar to those previously reported for graphite [7].

It is also evident from figure 3(a) that the even numbered clusters have greatest stability, and Smalley et al. [9] have proposed a likely formation mechanism to account for this phenomenon. Formation of the high even mass carbon cluster cations has been attributed to ion/molecule reactions that occur in the laser desorbed plasma. Highly reactive carbon radicals ranging in size from one to twenty atoms are initially desorbed from the sample. These then react with each other to form the larger more stable even numbered clusters.

The mass distribution of the anionic carbon clusters (Figure 3(c)) is similar to that observed from the graphite sample. It would, therefore, appear the same mechanism as that proposed for graphite [7] also accounts for the low mass range distributions from the three anthracitic coals.

Another important factor which has been observed to influence the laser ablation mass spectra is the laser irradiance time. Figures 3(a&b) and (c&d) show the effect of different laser irradiance times (200 µs) and 8 ns on the mass distributions of the cationic and anionic carbon clusters, respectively. It is believed that both the laser irradiance time and the molecular structure of the sample are important in determining the formation and mass distribution of the carbon clusters [7]. This is dramatically shown in the mass distributions of the cationic carbon clusters. The mass distribution produced at an irradiance time of 200 µs (Figure 3(d)) shows species up to \(C_{50}^+\), while that produced with an irradiance time of 8 ns (Figure 3(b)) shows only a few lower mass range carbon clusters. In contrast, the mass distributions of the anionic carbon clusters (Figures 3(c&d)) show only a small variation with different irradiance times.

The mass distributions from the laser ablation experiments on the lignite (Figures 4 (a&b)) are similar to those from the anthracitic coals. Again, the most intense and stable species in the mass distribution of the cationic carbon clusters, which range up to \(C_{150}^+\), is \(C_{60}^+\). Similarly, the mass distribution of
the anionic carbon clusters are, again also, below \( \text{C}_{25}^- \). Apparently, the mechanisms which generate the cationic and anionic carbon clusters from the graphite and the anthracitic coals are the same as those forming ionic carbon clusters from the lignite.

The irradiation conditions used in our laser ablation experiments did not produce large (i.e., \( n > 30 \)) carbon clusters from the graphite. However, no difficulty was encountered in generating these species from either the anthracitic coals or lignite. This observation suggests that more energy is required to break the highly ordered and strongly bonded covalent graphite lattice, than the structural components and linkages in coals.

CONCLUSIONS

1. A study of polynuclear aromatic hydrocarbons by FTMS has shown the viability of the technique for investigating surface species.
2. Cationic and anionic carbon clusters are generated from anthracitic coals and lignite.
3. Under the experimental conditions used in this investigation, the mass distributions of the cationic and anionic carbon clusters appear to be independent of coal rank, and similar to those previously reported for graphite.
4. The absence of \([\text{M+Na}]+\) adducts in the mass distributions from the coals means that the carbon clusters cannot be unequivocally considered as being desorbed from the coal surface, but more likely are formed in the gas phase by alternate ionization mechanisms.
5. The formation and mass distributions of the cationic carbon clusters are dependent on the laser irradiation time.
6. The potential of FTMS for studying carbonaceous materials, such as coals and graphite, has been demonstrated. Further developments in the technique should provide greater insight into the structure and nature of these materials.

REFERENCES

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<td></td>
<td></td>
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A - Pennsylvania State University sample bank; B - by difference; C - Analysis determined on a dry, mineral-matter-free basis; D - Analysis determined on a dry, ash-free basis.
Fig. 1. Positive ion laser ablation FT-mass spectra of the model compounds (doped with 1:1 NaCl) (a) Chrysene and (b) Fluoranthene at 1600 MW/cm² with an irradiance time of 8 ns.

Fig. 2. (a) Positive and (b) negative ion laser ablation FT-mass spectra of graphite at 70 kW/cm² with an irradiance time of 200 μs.
MODELING OF COAL STRUCTURE USING COMPUTER-AIDED MOLECULAR DESIGN

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Abstract
Knowledge of coal molecular structure is important in the understanding of coal reactivity. Computer-aided Molecular Design (CAMD) has been used to create and study 3-dimensional models of several postulated coal structures (Given, Wiser, Solomon, and Shinn). Using molecular dynamics calculations, a minimum-energy conformation for each structural model has been determined. Characteristics of the resulting coal structures will be discussed. Interactions of the structures with polar and non-polar solvent molecules are being explored to provide insight into coal pre-conversion chemistry. Future studies possible with this new tool will be outlined.

Introduction
The reactivity of coal is determined in substantial part by its chemical and physical structure. However, within any given coal there is considerable heterogeneity. Nonetheless, because of the strong link between structure and reactivity, there have been many attempts to model the macromolecular structure of various coals. For bituminous coals, the most widely accepted models developed during the past 30 years have been the aromatic/hydroaromatic structures, in which groups of about three aromatic rings, containing appropriate numbers and types of heteroatoms, are interconnected by hydroaromatic or aliphatic linkages (1-4). These models incorporate the average chemical and molecular characteristics of coal, and are not intended explicitly to represent actual "coal molecules". More recently, Spiro (5) has constructed physical space-filling models of several of these structures. Using the insight obtained from these models, he identified several steric difficulties in the original structures, and discussed the possible significance of the three-dimensional structures on mechanisms of coal pyrolysis.

Recently, computer-aided molecular design (CAMD) techniques have been developed to provide additional understanding of the structure and properties of complex molecular systems (6). Currently, CAMD techniques are being widely used in the pharmaceutical industry to guide the design and synthesis of a variety of biomolecules (drugs, enzymes, inhibitors, proteins). Using CAMD, one can not only construct a three-dimensional representation of a molecule, but can also convert the structure to an energy-minimized physical conformation, using molecular dynamics techniques. CAMD has been used to study basic coal structure (7), but not to examine the energetics of the structures. In this paper, CAMD is used to create three-dimensional models based on several postulated coal structures, and then to identify minimum-energy physical conformations for these models.

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Method

The CAMD studies described were carried out using BIOGRAF (BioDesign, Pasadena, CA), a software package for simulating organic and biological molecules. BIOGRAF allows the user to build molecules (structures), display them in a variety of formats (stick; dot surface; space-filling) and identify minimum energy conformations for them. The minimum energy conformations are found using molecular dynamics techniques with a suitable force-field approximation (6). In molecular dynamics, the energy of a structure is evaluated periodically as the atoms are allowed to move according to Newton's equations of motion at a specified "temperature" (which defines the atomic velocities). Dynamics runs usually involve many thousands of evaluation steps, representing the equivalent of many picoseconds of molecular motion. During the dynamics runs, structures twist and fold in ways which tend to optimize the non-bonded interactions (van der Waals, ionic, and hydrogen bonds), while maintaining appropriate bond lengths and angles.

BIOGRAF supports a number of force fields (AMBER, MM2, and DREIDING); in the current study, DREIDING was used. DREIDING is a very general force field that accounts for bond stretches and angles, torsions, and non-bonded interactions for a large number of atom types. Its accuracy is limited because it uses the same force constants for all atom types, although not for all types of interactions (i.e., the force constants for bond stretches are different from those for bending interactions, etc.). With this limitation, the energies calculated are most meaningful relative to one another, rather than in a quantitative sense. The BIOGRAF program was run on a MicroVAX II computer equipped with an Evans and Sutherland PS390 graphics terminal. The size of coal structures evaluated, and the duration of molecular dynamics runs, were limited by the available computing speed of this system (a 5000-step, 10-ps molecular dynamics run for a 1040-atom structure, with about 75,000 van der Waals interactions per step, required about 100 hours of computation).

Results

BIOGRAF was used to create three-dimensional models of four postulated bituminous coal structures, those of Given (1), Wiser (2), Solomon (3), and Shinn (4). After each of the models was created, it was converted into a minimum-energy physical conformation using molecular dynamics and energy minimization. Two of the structures, Given's and Shinn's, are shown in Figures 1 and 2. The Givens structure is shown because it has been widely cited as a possible representative coal structure. The Shinn structure represents the most complex coal structure in the literature, is also widely cited, and is similar in many ways to the Wiser and Solomon structures. Figures 1a and 2a show the two-dimensional molecular structures reported originally by Given and Shinn. These were used, with minor modifications, to create the computer space-filling models shown in Figures 1b and 2b (Given's structure was modified as suggested by Spiro (5) to eliminate a very strained quaternary carbon bond, and Shinn's structure was simplified by eliminating that fraction identified in his Table 5 as "residue", approximately 20% of the original structure). As the top and side views in Figure 2b show, the models are nominally two-dimensional at this point. Finally, Figures 1c and 2c show the minimum energy conformations adopted by the two models after 10-ps molecular dynamics runs. It is clear from the folding of these latter figures (especially Figure 2c) that simple two-dimensional representations probably do not adequately represent the coal structure. Significantly, the Given structure (Figure 1), constrained by pairs of methylene bridges between aromatic structures, is seen to be rather rigid. It did not change shape during molecular
dynamics as much as the Shinn structure, which folded up considerably due to van
der Waals and hydrogen-bonding interactions. The Viser and Solomon structures,
not shown, behaved much like the Shinn structure during energy minimization.

To evaluate further the CAMD results, a program was written to extract a number
of atomic and chemical parameters from each structure (number of atoms, fractions
of aromatic carbon and hydrogen, weight fraction of each atomic species,
empirical formula). The results were compared with the original literature for
each structure. This provided a useful check on the accuracy of the computer
models, which were rather complex (over 1000 atoms in the Shinn structure). In
all cases, the CAMD models compared favorably with the literature values.
Results of the computer analyses for the four structures analyzed are given in
Table I. The total numbers of atoms only appear as guides to the size and
complexity of each structure, and bear no relationship to the size of a "coal
molecule" or a decomposition product. The most significant difference between
the models appears to be in the values assumed for aromatic hydrogen. Given's
value is much lower than those of the other authors and is probably incorrect,
judging from more recent FTIR data (8). Given used pairs of methylene bridges
extensively to satisfy his low ratio of aromatic hydrogen, thus explaining the
major difference between his and the other structural models.

Also included in Table I is the minimum energy for each structure, calculated
during molecular dynamics runs in which the "temperature" was reduced over a 10-
ps period from 300 K to 10 K. In order to make the results more easily
comparable, the energies are expressed per unit atom. The Given structure is
energetically less favorable than the other three, because when it is considered
as an isolated structure, its relative rigidity allows only minimal van der Waals
and hydrogen-bond interactions. However, even if a number of Given structures
were made to interact, their rigidity would still allow less non-bonded
interactions, resulting in higher energy relative to the other structures. Thus,
the Shinn, Wiser and Solomon structures appear at this time to be the more
favored structures, based both on their more appropriate chemical characteristics
and on their observed structural flexibility and energetic advantages.

Discussion

Three-dimensional models of postulated coal structures have been created, and
minimum-energy conformations identified. For each of the three relatively
flexible structures modeled, there was actually a large number of slightly
different conformations with similar (low) energies. This suggests first that a
number of nearly-equivalent structures might be equally probable in coal, and
second, that structures with substantially lower energies than those identified
are probably not likely. Although the ring structures in the energy-minimized
Shinn structure (Figure 2c) show on the average no preferred orientation
(although some local stacking was observed), the macrostructure is still somewhat
anisotropic. If an extended structure based on the several units of the original
quasi-planar Shinn structure had been constructed and energy-minimized, the
anisotropy would have been more marked. This is in accord with Larson's
experimental observations (9) that vitrinite samples have essentially randomly
oriented organic groups (on a macroscopic scale), but at the same time show
highly anisotropic mechanical and solvent swelling properties.

This work represents a first use of CAMD techniques to model coal structure and
energetics. It has been possible to differentiate several postulated bituminous
coal structures based on their three-dimensional character and their energetics.
Obviously, these techniques could also be used to model coals of varying rank.
Modifications of the CAMD software are planned to allow the calculations of true and particle density of the coal structures. These density calculations will be especially important in the study of coal-solvent interactions, using both polar and non-polar solvents. Such studies should provide further insight into the nature of solvent swelling phenomena and the role of porosity in coal. Finally, although more difficult, it may be possible to model chemical interactions approximately using CAMD. In all, it appears that CAMD techniques represent a potentially very powerful new tool for studying the nature of coal structure and its effect on reactivity.

References

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TABLE I

COAL STRUCTURAL PARAMETERS (Weight Fraction DMHF)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Given</th>
<th>Wiser</th>
<th>Solomon</th>
<th>Shinn</th>
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<td># Atoms</td>
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<td>390</td>
<td>326</td>
<td>1040</td>
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<tr>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
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<tr>
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<td>0.014</td>
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<tr>
<td>S</td>
<td>---</td>
<td>0.053</td>
<td>0.026</td>
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<tr>
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Figure 1. Given structure. a) Structure from literature; b) Initial CAMD-generated structure; c) Energy-minimized CAMD structure.
Figure 2. Shinn structure. a) Structure from literature; b) Initial CAMD-generated structure, top and side views; c) Energy-minimized CAMD structure, top and side views (same orientation, same scale).
ABSTRACT

Since the earliest days of coal liquefaction processing and research, the desirability of correlation of coal properties with coal reactivity under direct hydroliquefaction conditions has been recognized by coal scientists. This article traces the history of reactivity correlations from the earliest work of Bergius through the classic work at the Bruceton Bureau of Mines during the 1940's to the most recent advances in this subject. Particular emphasis in this review is placed on an examination of the contributions of Professor Peter Given and his co-workers. Reactivity methodologies and techniques for correlation are presented and critically evaluated for utility and applicability as predictive tools.

Early Studies

The first attempts to hydrogenate coal in the laboratory were carried out by Marcellin Berthelot (1) in 1868. The results of subsequent experiments were published by Ipatiev (2) and his co-workers in 1904, in which it was demonstrated that the yield of liquids via high pressure pyrolysis of numerous organic constituents could be markedly enhanced by application of hydrogen. Emil Fischer suggested in 1912 that if coking operations were carried out in a hydrogen atmosphere, an increased yield of hydrocarbons might result. This hypothesis was later confirmed by Franz Fischer and Keller (3), who distilled a bituminous coal in hydrogen under pressure and found that the tar yield was significantly enhanced. Further research on coal hydrogenation was carried out by Fischer and his co-workers at the Kaiser-Wilhelm Institute using for the most part sodium formate and carbon monoxide in the presence of water (4).

Research which would eventually lead to the first "commercial" process for coal liquefaction was in progress as early as 1910 under the direction of Friedrich Bergius. Bergius initially studied the conversion of cellulose and peat in the presence of water, and only later turned his attention to coal. Coals were found to behave in a similar fashion, and Bergius was granted a process patent in 1914 for conversion of coal and other carbonaceous substances. Much of the work of Bergius is summarized in a document published in 1925 (5). In this paper, Bergius first describes the effect of the nature of the coal on the yield of liquid and tars from coal and states that coals
containing more than 85% carbon (d.a.f.) gave unacceptably low yields and were hence unsuitable for hydrogenation. In laboratory investigations on a series of 29 British coals of different rank (lignite through anthracite) published in 1928, Graham (6) indicated that no such arbitrary reactivity division was justified. Correlations for hydrogenation yields with coal properties were attempted by Graham using such factors as ultimate carbon, C/H ratio, C/(H-(O/8)) ratio, moisture, oxygen, and fixed carbon. All correlations were deemed to be unsuitable. Beuschlein and Wright (7) in a study of the hydrogenation of 14 U.S. coals and later Gordon (8) also reported similar findings. Francis (9) suggested that the reactivity of coal toward oxidizing agents was an excellent measure of their reactivity towards hydrogen.

MacroscoDic and Microscopic Coal Constituents
Bergius stated that fusain was the most difficult of the constituents of coal to liquefy. Shatwell and Bowen (10) reported the oil yield from a sample of hand-picked fusain from bituminous coal to be negligible. Wright and Sprunk (11) microscopically analysed the residues from batch hydrogenation of several different U.S. coals, and determined the relative reactivities of the various petrographic constituents. Both Gordon (12) and Heinze (13) stressed the need for reducing the fusain content of coals processed in continuous liquefaction plants in order to minimize handling problems in the solids/liquid separations unit operations. Other studies on the effect of the macroscopic properties of coal (vitrain, fusain, clarain, durain) were reported by Shatwell and Graham (14) and Horton et al. (15), with contradictory results.

The first systematic study on the effect of the macroscopic and microscopic coal constituents on coal reactivity was conducted at the Bruceton Bureau of Mines Research Station (now Pittsburgh Energy Technology Center of the US Department of Energy). An extensive treatise on the effect of the petrographic constituents on the reactivity of coal for direct hydrogenation was published by Fisher et al. (16) in 1942. As an integral portion of this research, the behavior of individual maceral groups was determined experimentally, and a correlation developed for liquefaction reactivity. A parity plot for predicted vs. actual yield of residue was presented by Fisher, where "residue" denoted the yield of acetone insolubles after reaction at 445 - 450 °C for 2 hours (initial hydrogen pressure of 2000 psi). Here, the yield of residue was predicted by assuming that the coal constituents would react as follows:

ash and fusain = 100% residue
opaque attritus = 38% residue
all other constituents = 0% residue

While this correlation was deemed to be more adequate than previous relationships based solely on rank or carbon
content, the deficiencies in terms of chemical differences between macroscopic and microscopic coal constituents for coals of varying rank was recognized by these researchers.

The Work of Peter Given
During the 1970's, Professor Peter Given and his co-workers at Penn State University began a very extensive study of the effect of coal composition on coal reactivity utilizing 104 coals from the U.S. To date, a series of ten papers have been published concerning the coal reactivity studies of Given et al., of which two pertain directly to the subject of reactivity correlations. The first paper (17) dealt with correlations between properties of 104 coals from the Penn State/DOE coal sample bank and conversion of coal to ethyl acetate solubles measured after reaction at 400 °C for one hour in tetralin. This paper introduced the concept of cluster analysis to the subject of reactivity correlation. It was reported that partitioning the samples into three distinct groupings (clusters) markedly improved the total variation accounted for by the multiple linear regression models employed for correlation of conversion and coal properties. The groupings recommended had the following characteristics:

- **Group 1:** medium sulfur, high rank
- **Group 2:** high sulfur, medium rank
- **Group 3:** low sulfur, low rank

The regression equations developed for correlation of liquefaction conversion and coal properties for each of these groups were as follows:

- **Group 1:** \( \text{Conv} = 34.8 \, R_o + 50.7 \, \text{H/C} + 0.16 \, V + 30.5 \)
- **Group 2:** \( \text{Conv} = 0.86 \, \text{VM} - 22.8 \, R_o + 1.39 \, S_t + 39.0 \)
- **Group 3:** \( \text{Conv} = 0.93 \, \text{VM} + 0.28 \, \text{TRM} - 1.7 \)

where: 
- \( R_o = \text{vitrinite reflectance} \)
- \( \text{H/C} = \text{atomic hydrogen-to-carbon ratio} \)
- \( V = \text{vitrinite content of coal} \)
- \( \text{VM} = \text{volatile matter} \)
- \( S_t = \text{total sulfur} \)
- \( \text{TRM} = \text{total reactive macerals} \)

The adequacies of these reactivity correlations, expressed as a percentage of the total variation in the data set explained by the model, were 80.0%, 79.2%, and 47.5% respectively. A later paper in the series (18) concentrated on the development of reactivity correlations for a set of 26 high volatile bituminous coals with high sulfur contents, and extended the models previously developed in include analyses of the liquefaction products and coal structural features. These structural features included the usual compositional parameters as well as data from FTIR, \(^{13}\text{C}-\text{nmr},\) and the products of oxidation with trifluoroperoxyacetic acid. No significant correlations between liquefaction yields and structural features of the coals were found from this study.
Reactivity Definitions

The traditional parameter that has been used for coal liquefaction reactivity correlations is the point-yield conversion. This parameter is defined by measuring the yield of some solvent-soluble material (THF, pyridine, toluene, etc.) at a fixed reaction time and fixed temperature. This single parameter has been widely utilized by many researchers as the dependent variable in reactivity correlations with coal properties such as volatile matter, H/C and O/C atomic ratios, vitrinite reflectance, maceral distribution, etc. (19,20,21,22,23,24,25,26). As has been recently demonstrated by Shin et al. (27), this parameter can provide meaningful correlations with coal properties for a narrow suite of reasonably homogeneous coals, but the correlations weaken significantly or even disappear if either the time or temperature is changed. Use of a rate constant as a correlational parameter for coal reactivity was proposed by Furlong (28) and Gutmann (29), and was found to be generally satisfactory for a particular suite of coals within a single rank. This parameter, however, also fails to hold if the temperature is changed (27). An attempt to derive a more universal parameter that could be employed for definition of coal reactivity was made by Shin et al. (30), who combined both static and dynamic reactivity parameters into a single variable.

Many of the compositional parameters utilized as independent variables in the work cited above represented derived coal properties rather than fundamental chemical features which, as pointed out by Neavel (31), limits their utility in correlational models. Instrumental techniques such as pyrolysis/mass spectrometry (32,33) $^{13}$C-n.m.r., FTIR, and $^1$H-n.m.r. have also been employed in an attempt to generate a larger data base of compositional information for use in correlation with reactivity. In some cases, the parameters developed from these data are derived from statistical techniques such as principal component analysis and factor analysis, and thus have little if any interpretation or meaning chemically. In this regard, the later work of Neill, Shadle, and Given (34) represents a significant departure from this philosophy in that an attempt was made to correlate both liquefaction chemical properties and coal structural features with the observed liquefaction reactivity.

The lack of significance often found with single-parameter reactivity models has been interpreted to reflect the need for development of multi-parameter models containing functional dependence for reactivity on several compositional parameters. Recently, the use of activation energy as a fundamental parameter for correlation of liquefaction reactivity data has been proposed. Prasad (35) collected reported values for activation energies from other studies, and found a direct correlation between...
hydroliquefaction activation energy and the H/C ratio of the coal. Shin et al. (36) measured the hydroliquefaction activation energies for conversion of 5 bituminous coals from the Argonne Premium coal collection to THF and toluene solubles. Correlation of these data with fundamental coal chemical properties as determined from $^{13}$C-n.m.r (CP/MAS with dipolar dephasing) and $^1$H-n.m.r. (CRAMPS) was successful in developing single parameter reactivity models with very high levels of significance (90%) between the following variables:

- $E_a$ (toluene) $\leftrightarrow$ total oxygen
- $E_a$ (THF) $\leftrightarrow$ aliphatic hydrogen
- $E_a$ (toluene) $\leftrightarrow$ protonated aliphatic carbon

**Observations and Conclusions**

Coal is an extremely heterogeneous material, both from a macroscopic and microscopic point of view. Correlation of liquefaction reactivity with coal properties is, as a result, inherently difficult and any truly "universal" correlations that will be developed will need to be based on fundamental coal chemical and structural information. Lack of this type of information has been a severe limitation for all of the correlational efforts cited in this brief review. If truly predictive models are to be developed, basic data on coal chemical properties will be invaluable. Choice of a reactivity definition employed as the dependent variable in these correlations is probably relatively arbitrary, and may be based totally on purely operational considerations (rate of reaction or extent of reaction) rather than any fundamental considerations. The role of pretreatment processes on reactivity modification (drying, grinding, etc) and mineral matter and matrix effects caused by organic/inorganic interactions needs to be better defined. This is especially true for low rank coals, where the inherently high reactivity of these materials can cause severe processing difficulties leading to artificially low levels of conversion.

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INFLUENCE OF ORGANIC COAL STRUCTURE ON LIQUEFACTION BEHAVIOUR UNDER LOW-SEVERITY CONDITIONS

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ABSTRACT

The influence of coal structure on primary conversions and oil yields in thermolytic extraction with different H-donor and non-H-donor solvents and in dry catalytic hydrogenation has been investigated. Pre-soaking of coal/H-donor solvent slurries at 250°C increased conversions and the level of hydrogen transfer at short contact times (SCT ≤ 10 min.) with 9,10-dihydrophenanthrene demonstrating the importance of solvent accessibility. However, contrary to other studies, prior removal of THF-extractable material (mobile phase) from one bituminous coal actually gave rise to higher conversions to pyridine-solubles for non-donor polynuclear aromatic compounds (PAC), such as naphthalene, phenanthrene and pyrene. These findings highlight the difficulties in relating primary conversions to coal characteristics. In contrast, oil yields have been found to broadly increase with decreasing rank in both H-donor solvent extraction with a process solvent and dry catalytic hydrogenation. However, in SCT tetralin extraction where poor physical contact between coal and solvent exists, neither total conversion nor oil yield correlates with rank.

INTRODUCTION

The correlation of coal characteristics with liquefaction behaviour has received considerable attention (see, for example refs 1-7) particularly since the renewed interest during the 1970s in the production of liquid fuels and chemical feedstocks directly from coal. As early as 1940, Storch and coworkers (8, 9) demonstrated that coals containing up to ~87% dmmf C give high yield of soluble products (albeit under severe conditions) and materials which today would be classified as vitrinite and inertinite liquefy readily. More recently, the work of the late Peter Given and coworkers (10, 11) on tetralin extraction of US bituminous coals is particularly noteworthy; high sulphur coals of intermediate carbon content gave the highest conversions. However, apart from the lack of precise structural information on the nature of aromatic, aliphatic and heteroatomic groups and low molecular weight (MW)
material (mobile phase) in coals, research has been hampered by the fact that the rate and extent of conversion are heavily dependent on the conditions used. Indeed, the recent review by one of the authors(9) indicated that a clear distinction has to be made between overall or primary conversions (typically pyridine, quinoline or THF-solubles) and distillate or oil yields (toluene or alkane soluble material). The profound influence of low MW material and the nature of H-donor and non-donor solvents on primary conversions were also highlighted. In contrast, distillate or oil yields often correlate with parameters reflecting the aliphaticity of coals (H/C ratio - ref. 5, decreasing vitrinite reflectance - ref. 6, CH2 content - ref. 7), better correlations being achieved for low-rank coals if yields are expressed on a "CO2 free" basis(5). The effects of coal characteristics on conversions are generally much less pronounced under high-severity conditions when a combination of vehicle solvent, hydrogen overpressure is catalyst are employed.

In this paper, a number of low-severity liquefaction regimes are considered. The influence of different H-donor and non-donor solvents on primary conversions without a hydrogen overpressure is discussed in the light of other recent work(10-12). Also, it is demonstrated that oil yields broadly increase with decreasing coal rank in both H-donor extraction and dry catalytic hydrogenation provided that retrogressive reactions are avoided in the initial stages of coal dissolution.

EXPERIMENTAL

Conditions used for the extraction and hydrogenation experiments are summarised in Table 1. H-donor solvent extractions of a Wyodak sub-bituminous coal (73% dmmf C), an Illinois No.6 coal (78% dmmf C) and a UK bituminous coal (Pt. of Ayr, 87% dmmf C) were conducted using (i) a Lummus process - derived distillate (nominal boiling range of 340 to 400°C) containing approximately 1% donatable hydrogen) as described previously (14) and (ii) tetralin with a short contact time (SCT, 10 min). The relatively high temperature of 450°C was used with the process distillate to achieve high oil yields without having a hydrogen overpressure.

To investigate factors affecting the initial stages of coal dissolution, extractions were conducted on two UK coals (Linby, 82% dmmf C and Pt of Ayr) at 400°C using a number of model compounds including tetralin, naphthalene, 9,10-dihydrophenanthrene, phenanthrene and pyrene for periods up to 30 min. For Linby coal, the effect of prior Soxhlet extraction with THF on conversions was investigated (extract yield, 6% daf coal). Also, coal/solvent slurries were pre-soaked at 250°C in a number of experiments. For the model hydroaromatic compounds, the amount of H transferred during extraction was determined by GC analysis of the products.

Dry hydrogenations with and without a dispersed sulphided molybdenum (Mo) catalyst (1% loading of Mo) were carried out at 350 and 400°C (15) (Table 1) on a suite of five coals comprising a Spanish lignite (Utrillas, 60.4% dmmf C), a sub-bituminous coal (PSOC-1408, 72.9% dmmf C), two h.v.A bituminous coals (PSOC-1266 and 1296, 83% and 87 dmmf C, respectively) and a l.v. bituminous coal (PSOC-1325, 90% dmmf C). To investigate the role played by low MW solvent extractable material (mobile phase) in dry catalytic hydrogenation, a series of experiments were conducted with Utrillas lignite and an Illinois No.6 coal in which the coals were first extracted with chloroform prior to catalyst impregnation. The quantities of chloroform-soluble material extracted were 2.5 and ~5.0% dmmf coal for the lignite and the bituminous coal, respectively.

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RESULTS AND DISCUSSION

Primary Conversions and Influence of Mobile Phase

Yields for the various H-donor and non-donor solvent extractions of Linby coal at 400°C are summarised in Table 2; the conversions for the THF-extracted coal include the extracted material. Surprisingly, pre-extraction with THF significantly increases primary conversions in the polynuclear aromatic compounds (PACs) investigated. These findings appear to be contrary to those of other liquefaction(16) and pyrolysis(17) studies where prior removal of chloroform-extractable material significantly reduced conversions. However, Rincon and Cruz(18) have reported recently that pre-swelling coals in THF increases conversions for both anthracene oil and tetralin. The fact that Pt. of Ayr (87% dmmf C) coal yielded over 80% pyridine-solubles in pyrene (C.E. Snape, unpublished data) without pre-extraction is consistent with the earlier results of Clarke et al (16) for anthracene oil extraction where UK coals containing ~85-87% dmmf C gave the highest conversions. It was suggested previously by one of the authors that this could correspond to a minimum in the cross-linking density of bituminous coals (1). However, these latest findings infer that the mobile phase is merely limiting accessibility for larger PACs, such as pyrene, within lower rank bituminous coals, such as Linby.

Conversions to pyridine-solubles for non-THF-extracted Linby coal were much greater with naphthalene than with phenanthrene and pyrene (Table 2, pre-soaking at 250°C has little effect on conversions) and, even after THF extraction, naphthalene conversions are comparable to those of pyrene. Although Neavel obtained high yields of pyridine solubles with naphthalene at short contact times for some US bituminous coals (20), conversions were much lower after longer extraction times. This trend is not evident for Linby coal where little variation in conversion to pyridine and THF-solubles is found for residence times between 10 and 30 min for both the initial and THF-extracted coal samples (Figure 1 and Table 2). The trends reported here were certainly not anticipated from previous studies with model PACs (17); however, yields of THF-solubles for pyrene were considerably greater than those obtained with both phenanthrene and naphthalene (Table 2, Figures 1 and 2). This evidence provides strong support for pyrene being an effective "hydrogen-shuttler" (20); the available hydrogen in Linby coal is utilised more effectively with pyrene than with naphthalene and phenanthrene, generating significantly higher yields of THF-solubles.

As expected, tetralin and 9,10-dihydrophenanthrene gave much higher yields of THF-solubles after THF extraction than the PACs with the exception of pyrene (Table 2). Pre-soaking the coal/solvent slurries at 250°C increased SCT conversions for 9,10-dihydrophenanthrene but not tetralin (Figures 3 and 4) presumably due to poorer physical contact of tetralin with the coal; Narain et al (22) found similar improvements in SCT hydroliquefaction with 1-methylnaphthalene. For 9,10-dihydrophenanthrene, the higher conversion to THF-solubles was not accompanied by an increase in H consumption. However, the conversion at SCT (Figure 3) was no more than that obtained after prolonged extraction (30 min, Table 2) with pyrene where no H donation can occur. This agrees with the work of Baldwin and coworkers (25) which showed that oil yields (dichloromethane – DCM; toluene or alkane-solubles) provide more reliable indicators of H utilisation than overall conversions to pyridine (or quinoline) or THF-solubles. The lower yields of pyridine-solubles obtained with tetralin compared to 9,10-dihydrophenanthrene (Table 2) and even to naphthalene and pyrene for the THF-extracted coal (Table 2, Figures 1 and 2) again are probably attributable to tetralin being largely vaporised at liquefaction temperatures. Indeed, different trends in primary conversion are evident for the SCT tetralin and the higher temperature process-solvent extractions (Table 3). The sub-bituminous coal (Wyodak) gives the highest yield of quinoline-insolubles with tetralin consistent with the general trend found in SCT hydroliquefaction by Whitehurst (1,24). In the case of the process solvent, yields of THF-insolubles increase with increasing rank (Table 3) although the trend is much smoother.
than could be realistically expected for a larger suite of coals. Nitrogen containing solvents, such as indoline have also been found to give significantly higher primary conversions for Wyodak coal (25) than tetralin, presumably due to the more effective disruption of hydrogen bonds in the coal. Clearly, solvents which provide good physical contact are essential to minimise retrogressive reactions particularly for low-rank coals.

In view of the compelling arguments recently put forward by McMillan and coworkers (12) in support of solvent-mediated hydrogenolysis, it is pertinent to consider whether chemical or physical factors for the different H-donors investigated are responsible for inefficient hydrogen utilisation and, in particular, whether different conversions are evident for a given level of hydrogen donation. Majchrowicz et al (26) demonstrated that by increasing the filling factor for tetralin in autoclaves so that more of the tetralin is in the liquid phase, conversions to THF-solubles increased but the level of hydrogen transfer remained constant. Table 2 indicates that when 0.5% daf hydrogen has been consumed, the yields of THF-solubles obtained with 9,10-dihydrophenanthrene are considerably higher than with tetralin. Also, the maximum obtainable yield of THF-solubles at 400°C is significantly higher for 9,10-dihydrophenanthrene (Figures 3 and 4). Despite the reservations over the use of THF-soluble yields as indicators of H utilisation, these findings clearly indicate that cleavage of relatively stable C-C bonds via hydrogen radical transfer occurs to a significantly greater extent in 9,10-dihydrophenanthrene.

The results summarised in Table 4 (27) suggest that removal of some of the mobile phase prior to dry catalytic hydrogenation does not adversely affect chloroform-soluble yields obtained at long reaction lines and, in the case of the lignite, the initial rate of conversion may actually be enhanced. Thus, the breakdown of the macromolecular network of coals is not strongly dependent on the presence of mobile species.

**Oil Yields**

Figure 5 gives the yields of chloroform-soluble liquid products obtained from the dry hydrogenation experiments at 400°C with the sulphided Mo catalyst. Table 3 lists oil and gas yields from the process solvent extractions at 450°C. In both regimes, oil yields (chloroform or n-heptane-soluble liquids) generally increase with decreasing rank. Again, the trends are probably much smoother than could be anticipated for a larger suite of coals. For lignites and sub-bituminous coals, it is probably more appropriate to express oil yields on a "CO₂ plus CO free" basis (5) (Table 3), a higher yield then being obtained for Wyodak sub-bituminous coal compared to Illinois No.6 coal in the process solvent extractions (Table 3). Reducing the hydrogenation temperature from 400 to 350°C amplifies the effect of rank on the yields of chloroform-soluble liquids (27) (Figure 6) because of the greater thermal sensitivity of low-rank coals. For catalytic hydrogenation, the trends would not be so acute in the presence of H-donor solvents where conversions tend to be considerably higher.

Although the yield of DCM-insolubles increases with increasing rank in SCT tetralin extraction (Table 3, Q1 + QS/DCM insols), the actual estimated yields of DCM-soluble liquid product are similar for Wyodak and Pt of Ayr coals even after correcting for the carbon oxides. Thus, retrogressive reactions encountered in SCT extraction with tetralin for Wyodak coal limit both primary conversions and oil yields. The relatively high concentration of solvent extractable material in Illinois No.6 coal may be responsible for this coal giving the highest oil yield in SCT liquefaction. Also, for dry hydrogenation without catalyst, oil yields do not correlate with rank (Figure 5), the sub-bituminous coal giving a significantly lower oil yield than one of the h.v.A bituminous coals. Thus, the catalyst is needed to limit retrogressive reactions by promoting cleavage reactions probably by hydrogen radical mediated hydrogenolysis(19). These findings are in broad agreement with trends obtained under typical SRC-II processing conditions (4) where addition of pyrite is needed to give high oil yields for low-rank coals and clearly show the importance of limiting retrogressive reactions in the initial
stages of liquefaction for low-rank coals.

ACKNOWLEDGEMENTS

The authors thank the US Dept. of Energy (Grant Nos. DE-FE22-83PC00811 and DE-AC04-76DP00789) and the Science and Engineering Research Council with British Coal (CASC studentship for N.W.S) for financial support.

REFERENCES


### TABLE 2 Primary conversions for Limby coal at 400°C

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Coal treatment</th>
<th>Time (min)</th>
<th>Yields (Pyridine sols.)</th>
<th>THF sols. (% daf coal)</th>
<th>Hydrogen consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>None</td>
<td>10</td>
<td>51</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>30</td>
<td>58</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THF-ext.</td>
<td>7</td>
<td>81</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>76</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>None</td>
<td>7,30</td>
<td>22</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THF-ext.</td>
<td>7,30</td>
<td>38</td>
<td>30</td>
<td></td>
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<tr>
<td>Pyrene</td>
<td>None</td>
<td>7,30</td>
<td>24</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THF-ext.</td>
<td>10</td>
<td>60</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>83</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>9,10 Dihydro-</td>
<td>THF-ext.</td>
<td>3</td>
<td>55</td>
<td>34</td>
<td>0.5</td>
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<tr>
<td>phenanthrene</td>
<td>*</td>
<td>30</td>
<td>88</td>
<td>83</td>
<td>3.1</td>
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<tr>
<td></td>
<td>Pre-soak</td>
<td>5</td>
<td>88</td>
<td>53</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>93</td>
<td>80</td>
<td>1.9</td>
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<tr>
<td>Tetralin</td>
<td>THF-ext.</td>
<td>7</td>
<td>38</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>*</td>
<td>30</td>
<td>76</td>
<td>65</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Pre-soak</td>
<td>7</td>
<td>43</td>
<td>35</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>75</td>
<td>66</td>
<td>1.3</td>
</tr>
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</table>

* % daf coal

### TABLE 3 H-Donor Solvent Liquefaction Results

<table>
<thead>
<tr>
<th>Coal</th>
<th>Pt of Ayr</th>
<th>Illinois No. 6</th>
<th>Wyodak</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCT Tetralin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oils</td>
<td>8</td>
<td>5</td>
<td>26</td>
</tr>
<tr>
<td>% daf</td>
<td>69</td>
<td>60</td>
<td>35</td>
</tr>
<tr>
<td>coal</td>
<td>20</td>
<td>32</td>
<td>(24)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process Solvent</th>
<th>THF insol.</th>
<th>THF sols/C7 insol.</th>
<th>C7 liquids</th>
<th>CO + CO2</th>
<th>C2–C5 gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>% daf</td>
<td>THF insol.</td>
<td>THF sols/C7 insol.</td>
<td>C7 liquids</td>
<td>CO + CO2</td>
<td>C2–C5 gases</td>
</tr>
<tr>
<td>coal</td>
<td>47.5</td>
<td>47.1</td>
<td>41.5</td>
<td>(47.5)</td>
<td>6.0</td>
</tr>
</tbody>
</table>

| Q1 = quinoline insolubles | Q5 = quinoline solubles | C7 = n-heptane | * = includes water | ( ) = "CO2 + CO" free basis | DCM = dichloromethane |

### TABLE 4 Influence of Chloroform Pre-extraction on Oil Yields (Chloroform-Soluble Liquids) in Dry Catalytic Hydrogenation at 400°C

<table>
<thead>
<tr>
<th>Reaction Time (Min.)</th>
<th>Utilities Light</th>
<th>Illinois No. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Pre-extracted</td>
</tr>
<tr>
<td>5</td>
<td>50.0</td>
<td>65.7</td>
</tr>
<tr>
<td>10</td>
<td>59.0</td>
<td>74.3</td>
</tr>
<tr>
<td>60</td>
<td>66.0</td>
<td>77.8</td>
</tr>
</tbody>
</table>

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Figure 1: Conversion of THF-extracted Linby coal with naphthalene at 400°C.
(a) THF - solubles
(b) Pyridine - solubles

Figure 2: Conversion of THF-extracted Linby coal with pyrene at 400°C after pre-soaking at 250°C for 1 hour.
(a) THF - solubles
(b) Pyridine - solubles
Figure 3  Conversion of THF-extracted Linby coal with 9,10-dihydrophenanthrene at 400°C to THF-solubles.
(a) Normal extraction
(b) After pre-soaking at 250°C for 1 hour

Figure 4  Conversion of THF-extracted Linby coal with tertrane at 400°C after pre-soaking at 250°C for 1 hour.
(a) THF-solubles
(b) Pyridine-solubles
Figure 5  Effect of coal rank and sulphided Mo. catalyst on yield of chloroform-soluble liquids in solvent-free hydrogenation at 400°C.

Figure 6  Influence of temperature and coal rank on yield of chloroform-soluble liquids in dry catalytic hydrogenation with a sulphided Mo. catalyst.
AN INVESTIGATION OF THE CHEMISTRY OF CATALYTIC PRELIQUEFACTION

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INTRODUCTION

Direct coal liquefaction processes which have been developed over the years have been based on the philosophy of high temperature homolytic cleavage of bonds to yield free radicals which are capped by hydrogen from the donor solvent or hydroaromatic structures in coals. While low rank coals offer the potential of high oil yields because of their small aromatic ring cluster size, it has been observed that under conditions optimized for bituminous coals, low rank coals appear harder to liquefy (1,2). For example, Derbyshire and Whitehurst (3) demonstrated that low rank coals produce very low conversions in short contact time liquefaction in a donor solvent or in long time liquefaction in a non-donor solvent. For low rank coals and lignites, it appears likely that crosslinking reactions associated with oxygen functional groups (4,5) occur before the homolytic cleavage reactions, and if not controlled, can limit the maximum conversion of coal to liquids.

It has been observed that in single stage coal liquefaction, bond breaking, crosslinking and hydrogen transfer reactions are carried out simultaneously. This does not enable each individual reaction to be optimized. Recent research on "temperature staged liquefaction" routes, exploring the effects of catalyst and solvent has been pursued using tubing bomb experiments at Penn State University by Derbyshire, Davis, Schobert and co-workers (6-12). The tubing bomb results (6) showed that liquefaction of a low rank coal at 350°C in naphthalene with a Mo catalyst resulted in improved yields with higher fractions of oils in subsequent liquefaction at 425°C.

The objective of this work was the identification and optimization of the beneficial preliquefaction chemistry through the application of advanced analytical techniques and theoretical models which have been previously employed to understand and predict coal pyrolysis and fluidity behavior. The analytical techniques include three methods to determine the functional group composition of the preliquefaction products: 1) Quantitative Fourier Transform Infrared (FT-IR) spectroscopy (13-16); 2) Cross-polarization-magic angle spinning (CP/MAS) NMR with dipolar dephasing (17-21); and 3) Thermogravimetric analysis with detection of the evolved products by FT-IR spectroscopy (TG-FTIR) (22,23); 4) Field Ionization Mass Spectroscopy (FIMS), a method to determine the molecular weight distribution of soluble products (24-27); and 5) Solvent swelling to determine the degree of crosslinking in the preliquefaction residue (28,29).

The theoretical model describes the break up of the coal macromolecular network under the influence of bond cleavage and crosslinking reactions using a Monte Carlo statistical approach (30-34). A similar statistical approach for coal decomposition using percolation theory has been presented by Grant et al. (35). Such statistical methods have been used for the inverse problem in the polymer literature, i.e., the formation of a macromolecular network by polymerization (36-40).

EXPERIMENTAL

SAMPLES - Samples of bituminous and subbituminous coal were provided by the Penn State Coal Sample Bank and the Argonne Premium Sample Bank. The Penn State coals were obtained undried and in lump form about 12 mm diameter and were crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size. The crushed coals were subdivided by riffling into a number of 10 g representative samples and sealed in vials under nitrogen. The Argonne coals were provided in sealed vials under argon. Properties of the coals are shown in Table 1.

Preliquefaction and Liquefaction Experiments - Preliquefaction and liquefaction experiments were carried out at Penn State University and at Advanced Fuel Research, Inc. The procedure was that described by Derbyshire et al. (6). The preliquefaction was carried out in a tubing bomb at temperatures between 275 and 350°C. Coal was impregnated with MoS2 catalyst and mixed in a
ratio of 1:2 with liquefaction solvent. In most of the experiments, naphthalene was selected as the solvent. Reactions were carried out in tubing bomb reactors of about 20 cm³ capacity which were heated by immersion in a fluidized sandbath.

Following preliquefaction, the bomb was cooled and vented to determine the gases evolved by volumetric measurement and gas chromatographic analysis. The solid and liquid products were worked-up to obtain the yields of insoluble residue (either chloroform or tetrahydrofuran (THF) insoluble), asphaltenes (hexane insoluble, THF-soluble) and oils (hexane-soluble). In these calculations, it was assumed that the naphthalene was part of the hexane solubles.

ANALYSES - Quantitative FT-IR Analysis - Selected samples of the liquefaction products, total product, the chloroform extracts, the asphaltenes, and the solid residues were analyzed as KBr pellets by FT-IR. The methods employed for quantitative analysis have been described previously (13-16).

TG-FT-IR - Pyrolysis analyses were performed on the preliquefaction solids using thermogravimetric (TG) analysis with on-line analysis of the evolved products (including an infrared spectrum of the condensables) by FT-IR. The TG-FTIR method has been described previously (22,23).

Solvent Swelling and Extraction - The residue samples were extracted with pyridine at the boiling point to obtain the amount and composition of the extract. A portion of the dried, extracted solids was swelled in pyridine in order to estimate the density of crosslinks introduced by the liquefaction process. The solvent swelling measurements were carried out according to the method of Green, Kovac, and Larsen (28,29).

FIMS Analysis - Selected extracts were sent for analysis in the Field Ionization Mass Spectrometry (FIMS) apparatus at SRI International. This technique was described by St. John, et al. (24) and has been used extensively in our development of the network model for coal decomposition (30-34,41,42). The Field Ionization induces little fragmentation and so provides a determination of the sample's molecular weight.

NMR - NMR analyses were performed on selected samples using dipolar dephasing and off magic angle spinning methods developed at the University of Utah (17-21). This work was performed at the University of Utah under the direction of Professor Ronald Pugmire.

Model Compounds - Model compounds were employed to provide well known materials to study specific chemical reactions or to provide standards to calibrate the analytical techniques. These included 1-naphthoic acid and 2-naphthoic acid to study the reaction of aryl carboxyl groups under preliquefaction conditions.

RESULTS

PRODUCTS DISTRIBUTION - Both the products of the preliquefaction and liquefaction stages were analyzed. Variations were made in coal type, (lignite, subbituminous, and bituminous), preliquefaction temperature (275-350°C), gases present (hydrogen, nitrogen, helium), catalyst (Mo or none), solvent (naphthalene, tetralin or dry) preliquefaction time (30 min - 60 min), and liquefaction time at 425°C (10 min - 30 min). Results for PSOC 1401 (a Wyodak subbituminous, which was the most frequently studied coal) are presented in Fig. 1. The figure compares liquefaction data (10 min at 425°C) for no preliquefaction, preliquefaction at 275°C (with H₂ and catalyst) and preliquefaction at 350°C (with H₂ and catalyst). The results show that preliquefaction at 350°C does have a positive effect on the total yield and product quality in liquefaction (much lower residue) while preliquefaction at 275°C causes a negative effect (higher residue). The results for other coals and conditions are summarized as follows:

1) Preliquefaction at 275°C appears to have a negative effect on subsequent liquefaction when compared to results without a preliquefaction step. Preliquefaction results in up to 10% of the coal converted to gases and chloroform solubles. Most coals behaved the same and there was little effect due to the presence of either the catalyst or hydrogen.
The solvent was, however, necessary to produce the chloroform extracts as none were produced by a thermal treatment in the absence of a solvent.

2) Preliquefaction at 350°C in the presence of a catalyst appears to have a strong positive effect on liquefaction for low rank coals. The largest change due to preliquefaction (high chloroform extract yield, high CO₂ yield) is produced by both hydrogen and catalyst. Nitrogen and catalyst produce smaller but similar changes, while no catalyst produces much less change and as shown by Derbyshire et al. (6) produces little change in liquefaction. Preliquefaction with no solvent or catalyst produces the least change in the product. Preliquefaction in tetralin produces no improvement over preliquefaction in naphthalene.

**FT-IR FUNCTIONAL GROUP ANALYSIS** - Quantitative FT-IR functional group analysis was performed on the starting coals, preliquefaction residua, chloroform extracts, oils, and asphaltenes.

**Residua** - Results for PSOC 1401, preliquefaction with H₂ and Mo at 350°C, are presented in Fig. 2. The preliquefaction step produces the following changes: 1) decreases the carbonyl (1700 cm⁻¹) and hydroxyl regions (3400 cm⁻¹) (presumably carboxyl loss); 2) decreases the aliphatic hydrogen (2900 cm⁻¹); and 3) substantially increases the aromatic hydrogen (750-850 cm⁻¹).

The quantitative functional group analysis for PSOC 1401 from these and other spectra are summarized in Fig. 3 and Table 2. The aliphatic hydrogen (Fig. 3a) is found to decrease for solvent treated residues compared to residues formed in the absence of the solvent. The most drastic changes are in the aromatic hydrogen (Fig. 3b), the carbonyl (Fig. 3e), and the one adjacent aromatic hydrogen (Fig. 3g). As can be seen, the major changes are brought about with the catalyst and solvent. These are changes which presumably lead to the improved liquefaction yields.

There are three other cases of interest. The first is HCD 1401-350° which is identical to HC 1401-350° in using hydrogen and a catalyst but no solvent was present. The quantitative functional group analysis is presented in Table 2. It shows the loss in aliphatics and carboxyl, but not the same dramatic increase in the aromatic hydrogen. The second case is NCT 1401-350 which was preliquefied in tetralin with a catalyst under a nitrogen atmosphere. The results in Table 2 are very similar to HC 1401-350 (low aliphatics and low carboxyl). The third case is for the HC 1401-350 residue after it was subsequently heated to 400°C. This was done to see whether the high aromatic peaks are due to adsorbed naphthalene. The data in Table 2 show that the functional group composition is almost identical to that in the starting residue. So heating to 400°C does not change the chemistry and adsorbed naphthalene is not likely.

Our initial conclusion from the FT-IR data on the residua is that it is the reduction in the carboxyl concentration which is most important to the improvements brought about by preliquefaction, and this reduction requires the catalyst but not the solvent and probably not the hydrogen. The major reasons for these conclusions are: 1) pretreatments dry, with naphthalene (with hydrogen and nitrogen) and with tetralin, all reduced the carboxyl concentration, and the dry and naphthalene cases both produced improved liquefaction yields; 2) the presence of hydrogen does not appear to make much difference between HC 1401-350 and NC 1401-350; and 3) the increased aromatics were not present in the dry preliquefaction residue (HCD 1401-350) and so, do not appear necessary for the improvement in liquefaction.

The increase in the aromatic hydrogen appears to result from added naphthalene for the following reasons: 1) the peak positions are consistent with added naphthalene; 2) the increase is too large to have come from conversion of aliphatic hydrogen to aromatic hydrogen, no increase was seen for NT 1401-350 which had a similar decrease in aliphatic hydrogen; 3) increased aromatic hydrogen due to removal of the carboxyls would not be likely to increase the one adjacent hydrogen peak; and 4) the peak must be due to a tightly bound chemical because it is not removed at 400°C.

**Extracts** - Quantitative spectra were obtained for the soluble products of the preliquefaction process. Results for the THF extracts of the residue (asphaltenes 1) for HC 1401-350 is presented in Fig. 4 and Table 2. The asphaltenes are very high in carboxyl groups, methyl groups, and aliphatic or
hydroaromatic hydrogen. The spectrum does not show very large aromatic peaks; the material appears to contain less than 50% aromatic carbon based on the amount of aliphatic carbon and oxygen present. The THF solubles appear to have carboxyl concentration comparable to the original coal but much larger than the residue. They contain significantly less ether oxygen.

TG-FTIR ANALYSIS - The analysis of the volatile products are related to the functional group composition of the sample, so the TG-FTIR analysis provides a good complement to the FT-IR functional group analysis. Since the FT-IR analysis showed the carbonyl region to change drastically in preliquefaction, we consider the CO₂ evolution which results from the thermal decomposition of the carboxyl groups. Figure 5 compares the CO₂ evolution from a number of residua. The major change occurs for the catalytic preliquefaction at 350°C (HC 1401-350 and NC 1401-350). Here a drastic reduction is observed in the CO₂ evolution at all temperatures. This suggests a major chemical change in the carboxyl groups. The nitrogen thermal case shows less of a change.

SOLVENT SWELLING - The results showed that there was less or comparable loss in solvent swelling for a catalytic preliquefaction compared to thermal treatment without a catalyst. But since the catalytically treated samples show much greater removal of the carboxyl groups, these samples will undergo much less crosslinking upon further thermal treatment.

FIMS ANALYSES - FIMS analyses were performed on the extracts from HC 1401-350 which were separated into hexane solubles (oils plus naphthalenes) and hexane insoluble, THF soluble (asphaltene 2). The oil fraction is very volatile with an average molecular weight of 303 AMU on a number average basis. The results show that there is significant chemistry going on involving naphthalene dimerization and probably adduction.

NMR ANALYSIS - NMR analysis was performed on the residue from HC 1401-350. The results are presented in Table 3. The data confirm the lower aliphatic content and higher aromatic content in the preliquefaction samples determined in FT-IR. The increase in the aromatic content is in protonated carbon (0.28 for the residue compared to 0.17 for the coal). The major decrease in the aliphatics is in the CH₂ groups (0.27 in the coal vs. 0.16 in the residue). The cluster size in the preliquefaction coal (12.3 carbons) appears to be higher than for the raw coal (9.7). The carboxyl carbon (F₂) in the preliquefaction product (0.05) is also lower than in the raw coal (0.08) consistent with the FT-IR and TG-FTIR results.

STUDIES WITH MODEL COMPOUND - Since the results of the preliquefaction experiments with a subbituminous coal at 350°C in the presence of a catalyst showed a significant role of carboxyl groups in preliquefaction chemistry, model compounds with aryl carboxyl groups (1-naphthoic acid and 2-naphthoic acid) were studied. The preliquefaction was carried out at 350°C for 1 hour in nitrogen with ammonium tetrathiomolybdate (1% Mo on dmmf basis) as the catalyst. The starting reaction mixture used was 50% naphthalene, 25% of 1-napthoic acid and 25% of 2-napthoic acid (weight basis). The FT-IR spectra (dry, uncorrected) of the starting reaction mixture and the residue after preliquefaction were compared. There is a strong loss in the carboxyl and hydroxyl bands due to the loss of carboxyl groups during the preliquefaction in the presence of the catalyst. A blank run was done without the catalyst which indicates that the catalyst is necessary to cause excessive decarboxylation. The CO₂ formation was more than a factor of three higher, due to the presence of the catalyst. The CO₂ evolution in absence of the catalyst is due to the higher decarboxylation.

MODELING

The liquefaction model is based on AFR's FG-DVC model of coal devolatilization (30-32). The model describes the decomposition or condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions. Our model employs a sample macromolecular network in the computer consisting of aromatic ring clusters (monomers) linked by bridges. The bridges are either broken by bond scission reactions or are formed by crosslinking. In the model, the break-up or solidification of the molecule occurs near a "gel point" where the number of unbroken bonds per ring cluster (monomer), α, reaches a critical value α₂ = 0.95. For bituminous coals, this critical value can be achieved in pyrolysis and the coal melts and becomes fluid. The effects of low temperature crosslinking which occurs for low rank coals is to increase α so that is some cases the network

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cannot come apart by normal pyrolytic reactions.

For liquefaction, the hydrogen consumption in the pyrolysis process (which required hydrogen donation from the aliphatic and hydroaromatic hydrogen in the coal) was modified to allow donation from the solvent. In addition, the external and internal transport steps in devolatilization (which describe vaporization of small molecules and gas phase transport) are modified to describe small molecules becoming liquid and mixing with the solvent. The details of AFR's FG-DVC model can be found in Ref. 32.

From the analysis of the results on the preliquefaction chemistry, it was found that the preliquefaction process results in reduction of carboxyl groups, partial crosslinking of the structure and some bond breaking resulting in higher chloroform extractables. The effect of this preliquefaction process on subsequent liquefaction is high yields of liquids.

The preliquefaction chemistry and its effect on subsequent pyrolysis were simulated by the FG-DVC model. The starting polymer structure of Wyodak coal was modified by putting additional crosslinks (0.13/monomer) to account for partial crosslinking of the structure. The original coal had pyridine solubles of 7.4% but the residue after preliquefaction has THF solubles of 21.5%. To account for this change in the molecular weight distribution of the starting polymer, the oligomer length was decreased from 10 to 4. The donatable hydrogen was kept constant in both cases. The carboxy content (responsible for early crosslinking) was reduced from 6.9% to 2.9%. The results of the simulation are shown in Fig. E.

Comparing Figs. 8a and 8c for the original and modified coals respectively, we find that while the number of bonds/bead $\alpha$ for the unmodified coal do not go below the critical value of 0.95, the value of $\alpha$ for the modified coal does. This results in the opening of the macromolecular structure and better penetration of the liquefaction solvent in subsequent liquefaction resulting in high liquid yields. Figures Bb and Ed compare the fluid fraction of the mixture on pyrolysis at 440°C for original and modified coals respectively. The modified coal shows a much higher fluid fraction which results in greater fluidity during subsequent liquefaction.

**DISCUSSION**

There are three suggested modifications which could lead to improved liquefaction. They are: 1) reduced crosslinking; 2) hydrogenation; and 3) increased bond breaking. The experimental results suggest that modification 1 is the most likely, 2 does not occur and 3 appears to happen to some extent.

Having identified the probable chemical changes responsible for improvements in yield and quality in liquefaction, attention was focused on the reactions which produce the chemical changes. The results raise the following questions and possible answers.

**Question 1.** What is the chemistry of carboxyl removal? Partial answer. There are carboxyls removed from the residue by conversion to $\text{CO}_2$ and with the extract. This occurs only in the presence of the catalyst but with or without the solvent or hydrogen. Fewer crosslinks are formed than would otherwise have been formed with the amount of carboxyl removed. This is confirmed by FT-IR, TG-FTIR, NMR, the model simulation, and experiments with model compounds. Naphthalene adduction could have occurred in the HC 1401-350 case to produce the high aromatic, but carboxyl removed occurred in other cases without this effect. Most of the carboxyl removed is by the formation of $\text{CO}_2$. Decarboxylation is seen for the model compounds in the presence of the catalyst.

**Question 2.** What happens to aliphatics? The most probable answer. There is a reduction in the aliphatics, most likely produced by removal (with the chloroform solubles) of long chain polymethylene and small fragments high in methyl. This is confirmed by FT-IR, TG-FTIR, and NMR.

**Question 3.** Where do the increased aromatics come from? The most probable answer. Large increases in aromatics were observed in some cases, which are probably due to naphthalene...
adduction. Conversion from aliphatics is unlikely. The evidence comes from FT-IR, NMR, FIMS and the model compound studies which show that naphthalene adduction occurs.

Question 4. What kind of bonds hold the preliquefaction insoluble products together? The most probable answer. The bonds remaining in the residue appear similar to those in the parent coal based on the liquefaction and TG-FTIR data. But there is no really good experiment which determines the kinds of bonds. Based on the FT-IR spectra of the residue there is enough aliphatic hydrogen for \(-\text{CH}_2-\text{CH}_2-\) bonds.

Question 5. Why is the preliquefied insoluble product so easily liquefied? The most probable answer. The preliquefaction product with the reduced carboxyl groups content is more easily liquefied than the parent coal. Based on the product distribution and solvent swelling data and the model simulation, this improvement results from a reduction in the CO\(_2\) associated crosslinks and from the bond breaking which produces the chloroform solubles. Both effects reduce the total number of bonds linking the network so that the coal can become fluid. If the chloroform soluble fraction is removed after preliquefaction and the residue liquefied, the drastic improvement in the liquefaction is not observed. The model simulation confirms that the residue alone will liquefy slightly better than the parent coal, but not as good as the mixture.

CONCLUSIONS

1) Preliquefaction of a Wyodak subbituminous coal at 350°C with solvent, catalyst and hydrogen produced the best results, (highest yields and best quality) in subsequent liquefaction for 10 minutes. The preliquefaction step produced substantial changes in the functional group composition of the residue, (low aliphatic, low carboxyl, and high aromatic), a large chloroform extract yield and a high CO\(_2\) yield.

2) Other preliquefaction treatments at 350°C produced results which were not as good as the best case.

3) The preliquefaction step did not appear to induce appreciable hydrogenation of the residue even with toluene as a solvent or a hydrogen gas atmosphere.

4) The improvement in liquefaction behavior appears to be due to loss of the functional groups usually responsible for crosslinking without the associated crosslink formation; probably carboxyl.

5) Experiments were carried out to test whether carboxyl groups on a model compound were removed under preliquefaction conditions (350°C, Mo, naphthalene solvent and nitrogen or hydrogen gas). Results showed that almost all of the carboxyl groups were converted to CO\(_2\). Almost no decarboxylation occurred in the absence of the catalyst.

6) Simulations show that the reduction in the carboxyl group concentration in the preliquefaction step for the Wyodak coal is capable of significantly enhancing the subsequent decomposition of the macromolecular network in the liquefaction step, thus improving the liquefaction yields.

REFERENCES


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Figure 1. Product Distributions for Preliquefaction and Liquefaction Comparing Results for No Pretreatment, Preliquefaction at 275°C and Preliquefaction at 350°C. P = Pretreatment and L = Liquefaction. Liquefaction Conditions - 425°C, Mo, Catalyst, Naphthalene Solvent, Hydrogen, Atmosphere (10 min.). Preliquefaction Conditions - Mo, Catalyst, Naphthalene Solvent, Hydrogen, Atmosphere (275°C - 30 min., 350°C - 60 min.).

Figure 2. Comparison of FT-IR Spectra for Residue and Parent Coal for PSOC-1401 Wyodak Subbituminous Coal.

Table 1 - Coal Properties.

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**Nomenclature**
- HO - Hydrogen Catalytic
- NC - Nitrogen Catalytic
- HT - Hydrogen Thermal
- NT - Nitrogen Thermal
- HCD - Hydrogen Catalytic Dry
- HeD - Helium Dry
- Tet - Tetralin
Figure 3. Variations in Functional Group Compositions with Preliquefactions.
Figure 4. Comparison of FT-IR Spectra of THF Extracts of the Residue (Asphaltene) Formed at 350°C in the Presence of Catalyst and the Presence of Hydrogen.

Table 3 - Carbon Structural Distribution of the Wyodak Subbituminous Coal and the Pretroleum Residue Formed at 350°C in the Presence of Catalyst and Hydrogen

<table>
<thead>
<tr>
<th>Sample</th>
<th>$f_a$</th>
<th>$f_a^C$</th>
<th>$f_a^H$</th>
<th>$f_{al}^H$</th>
<th>$f_{al}^*$</th>
<th>Carbons/Clusters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>.63</td>
<td>.08</td>
<td>.17</td>
<td>.37</td>
<td>.27</td>
<td>9.7</td>
</tr>
<tr>
<td>Char</td>
<td>.75</td>
<td>.05</td>
<td>.28</td>
<td>.25</td>
<td>.16</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Fractions of sp$^2$ hybridized carbon and (error estimate).
$f_a$ = total carbon, (±0.03).
$f_a^C$ = carbonyl - δ > 165 ppm, (±0.02).
$f_a^H$ = protonated and aromatic, (±0.03).
Fraction of sp$^3$ hybridized carbon and (error estimate).
$f_{al}$ = total carbon (±0.02).
$f_{al}^H$ = CH or CH$_2$, (±0.02).
$f_{al}^*$ = CH$_3$ or nonprotonated, (±0.03).

Figure 5. Comparison of CO$_2$ Evolution Profiles for PSOC-1401 Samples of Coal and Pretroleum Residue at 350°C from the TG-Plus.

Figure 6. Comparison of Number of Bonds per Bead for a) Original Wyodak Coal (initial crosslinks = 290, initial extract yield = 7.4%, oligomer length = 10 and hard bonds = 200) and c) Modified Wyodak Coal (initial crosslinks = 600, initial extract yield = 21.5%, oligomer length = 4 and hard bonds = 0). b and d Compare the Fluid Fraction and Extract Yield for Original Wyodak Coal and Modified Wyodak Coal, Respectively.
Reactions that occur during preconversion processing of coal in direct liquefaction can be either beneficial or harmful. If the thermally or catalytically produced fragments are rapidly stabilized with hydrogen, the resulting compounds have lower molecular weights than the original coal molecules and can be easily upgraded. However, if stabilization is inefficient, the fragments can undergo retrogressive reactions resulting in formation of higher molecular weight materials that are more difficult to upgrade. In current Wilsonville integrated two-stage direct coal liquefaction processes, the initial reactions of coal, which are grouped together under the term preconversion chemistry, occur between the time the coal is mixed with recycle solvent and the time the coal slurry enters the first-stage reactor. This includes the preheating step in which the coal slurry is heated up to first-stage reaction temperatures. The initial temperature for preconversion processing is about 180°C (the temperature of the solvent-coal mixture in the slurry blend tank). The final temperature has not been reported because the temperature of the feed to the first-stage reactor is proprietary. However, it must be less than the average first-stage temperature, which is approximately 425°C.

The objectives of this work are to identify the types of compounds and process conditions that give rise to retrogressive reactions during preconversion processing. Experiments have been performed to evaluate the impacts of temperature, catalysts, mineral matter, and hydrogen donors on these reactions. Initial studies have been carried out using dibenzyl ether (DBE) because ether linkages represent one type of bonding believed to be present in coal (1). Previous studies have analyzed the kinetics and mechanism of thermolysis of DBE (2,3) and have also used DBE to study effects of process variables in coal liquefaction (4). Results of thermal reactions with DBE have shown that the main reaction products are toluene, benzaldehyde, benzyl alcohol and benzene (2). In the presence of catalysts such as ZnCl₂, the product distributions are more complicated and can contain significant amounts of material with higher molecular weights than DBE (5,6).

EXPERIMENTAL

Materials
The commercial hydrotreating catalyst for these experiments was Shell 324M, a NiMo/Al₂O₃ catalyst with 12.4 wt% Mo and 2.8 wt% Ni. Prior to use, this catalyst was presulfided with a 10 mol% H₂S/H₂ mixture at 380°C and atmospheric pressure for 2 h, and was then

This work supported by the U.S. Dept. of Energy at Sandia National Laboratories under contract DE-AC04-76DP00789.
ground to -200 mesh. ZnCl₂ was used as received. Three types of fine-grained mineral matter were also utilized in experiments: mineral matter separated from an Argonne Illinois #6 Premium Coal by low-temperature ashing, kaolinite (Al₂Si₂O₅(OH)₄) in the form of a Georgia kaolin, and an acid-cleaned pyrite sample from the Robena mine.

**Hydrotreating Experiments**

Hydrotreating experiments and thermal reactions with dibenzyl ether (DBE) were performed in 26 cm³ batch microreactors with 1000 psig H₂ cold charge pressure. All reactions were performed for 15 minutes at temperatures of 180°C, 230°C or 300°C. The catalytic reactions were carried out both with and without the addition of a hydrogen donor (hexahydropyrene, H₆Py) or a hydrogen donor precursor (pyrene). Reactant and catalyst loadings for most experiments consisted of about 100 mg DBE, 50 mg catalyst or mineral matter, and 50 mg of pyrene or H₆Py. One set of four experiments at 300°C, which was aimed at determining the impact of clays on retrogressive reactions, had 425 mg DBE and kaolinite loadings ranging from 26 to 207 mg.

**Product Analyses**

Products from the microreactor experiments were dissolved in CS₂ and analyzed using a combination of gas chromatography (GC) and GC/mass spectrometry (GC/MS). Recoveries of products from several runs were determined quantitatively by GC using dodecane as an internal standard and response factors determined for DBE, toluene, pyrene and H₆Py. Recoveries of products from the DBE reactions included quantitation of all non-solvent and non-pyrene peaks that were detected on the gas chromatogram. Quantitation of the recoveries of pyrene and H₆Py included all detectable hydrogenated pyrene species. The amount of high molecular weight material formed by retrogressive reactions in each run is defined in this work as the amount of material that could not be detected by GC.

**RESULTS and DISCUSSION**

Products of the reaction of DBE that were identified in these 300°C experiments include toluene, which is the main product, benzaldehyde, benzyl alcohol, dibenzyl, and other C₁₄H₁₄ compounds, and diphenylmethane. No gaseous hydrocarbon products were detected in these runs.

Results of experiments performed at 300°C with Shell 324M are shown in Table 1. Two thermal runs at 300°C with DBE yielded some reaction, giving average values of 86 wt% unreacted DBE, 4 wt% toluene, 4 wt% benzaldehyde, 1 wt% benzyl alcohol, and 5 wt% material (100% minus total recovery) that could not be vaporized in the GC, thus showing the presence of high molecular weight material formed by retrogressive reactions. A similar reaction with Shell 324M as a hydrotreating catalyst gave 27 wt% toluene and no detectable DBE. The total recovery of products derived from DBE for this reaction was only 46 wt%. Therefore, 54 wt% of the reaction products were high molecular weight materials. When pyrene, a hydrogen donor precursor, was added to a reaction with Shell 324M (run 3), the toluene yield doubled compared to run 2. However,
23 wt% of the reaction product was still comprised of high molecular weight material. Addition of H₆Py instead of pyrene gave increases in toluene yield and DBE product recovery compared to pyrene addition. Even with this good hydrogen donor present at the start of the reaction, 17 wt% of the DBE product could not be detected by GC. The recoveries of all detectable pyrene species from experiments 3 and 4 were significantly less than 100%, suggesting an interaction between these compounds and either DBE or products derived from DBE.

Reactions were also performed with ZnCl₂ as a catalyst at 300°C with and without pyrene or H₆Py. These reactions all gave almost complete conversion of DBE, but the GC patterns showed very little intensity. Thus, the recoveries of products derived from DBE and the recoveries of pyrene and H₆Py (including all hydrogenated pyrene species) were low (<10 wt%) indicating the formation of more high molecular weight material than obtained in runs with Shell 324M. A GC/MS analysis of the products from experiments with ZnCl₂ plus pyrene and ZnCl₂ plus H₆Py showed the presence of peaks with molecular weights of 292 and 298, respectively, suggesting the presence of benzylpyrene and benzyl-H₆Py compounds, respectively. These identifications are supported by previous work (5), using DBE and toluene, in which benzyltoluene was identified as a product. If all the unrecovered pyrene (from the ZnCl₂ plus pyrene run) was converted to a benzylpyrene compound, the weight of the benzyl group present in this compound would only account for about 25% of the unrecovered DBE products. The same holds true for the reaction with H₆Py.

If these benzylation compounds are also present in the products for reactions 3 and 4 (Table 1) with Shell 324M, the weight of benzyl groups tied up in the benzylpyrene and benzyl-H₆Py compounds would account for 14 wt% additional recovery of DBE products in run 3 and an additional 6 wt% for run 4. Thus the total recoveries of DBE products would be about 90 wt% for these two reactions, suggesting that up to 10 wt% of the product could be due to high molecular weight material not detected by GC. However, elemental analyses of the catalysts are not yet available and may show that some of the missing material has been deposited on the catalyst.

GC analyses of the experiments with mineral matter separated from the Illinois #6 Premium Coal Sample only accounted for about 9 wt% of the amount of DBE in the feed. Coal-derived mineral matter contains many different components, including clays, pyrite (FeS₂), quartz and carbonates. Therefore, additional experiments were performed with pyrite and kaolinite to determine the impact of these two components on DBE. Pyrite was chosen because it has known catalytic activity. Kaolinite was chosen because it is a clay mineral present in coal and clays usually are the most abundant minerals in coal. In addition, a previous study (7) has shown that the acidic components of coal mineral matter enhance DBE conversion. The products of the reaction with pyrite have not yet been quantified, but the GC area counts suggest that pyrite gave a high recovery of DBE products and a toluene yield similar to those obtained with Shell 324M in runs 3 and 4 of Table 1. In contrast, a reaction with kaolinite gave a recovery of DBE products of only 7 wt%, suggesting that the clay components of the mineral matter are primarily responsible for the retrogressive reactions that occur.

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All of the products from the DBE experiment with kaolinite were soluble in CS₂. Filtration and weighing of the kaolinite from the reactor gave a good recovery with only a minor weight gain, which accounted for <2.5% of the non-recovered material. In addition, evaporation of the CS₂ from the reaction products yielded most of the weight that could not be detected by GC. Therefore, the poor recovery of DBE products had to be due to formation of high molecular weight materials. A set of four reactions was performed with different feed/kaolinite ratios. The results, shown in Table 2, indicate that even small amounts of clay can have a significant impact on recovery and hence on the formation of compounds by retrogressive reactions.

At 230°C, a thermal reaction and reactions catalyzed by Shell 324M, ZnCl₂, and mineral matter from the Illinois #6 coal gave results similar to those obtained at 300°C; pyrite yielded only about a third the toluene of the 300°C reaction.

At 180°C, a thermal run showed very little reaction and had a total recovery of 100 wt%. A reaction with Shell 324M gave 73% recovery of products derived from DBE including 55 wt% toluene. Comparison of these results with those of run 2 in Table 1 shows that the toluene yield is double that obtained at 300°C and the overall recovery is about 50% higher. The reaction with Shell 324M therefore appears to be more efficient at the lower temperature, and suggests that it would be beneficial to measure the rates of the reactions occurring at both 300°C and 180°C. Pyrite gave very little reaction at 180°C, which is not surprising since the pyrite–pyrrhotite transition does not occur at this low temperature and pyrrhotite is believed to be the active phase (8). A reaction with a feed containing 2:1 DBE:kaolinite gave only 15 wt% recovery of DBE products. Therefore, even at this low temperature, retrogressive reactions yielded 85 wt% high molecular weight products with kaolinite.

CONCLUSIONS

The results of these experiments indicate that retrogressive reactions of DBE occur in the presence of a good hydrogenation catalyst (Shell 324M), a Lewis acid (ZnCl₂), and coal-derived mineral matter. ZnCl₂, coal-derived mineral matter, and kaolinite (a clay present in coal) cause the greatest yield of high molecular weight products from retrogressive reactions. These results suggest that detrimental reactions can occur in the low temperature initial stages of coal liquefaction when coal mineral matter is present. Although the amount of retrogressive products is less in reactions with Shell 324M, it is still significant even with a good hydrogen donor and high pressure hydrogen. Therefore, the addition of a hydrogenation catalyst, such as Shell 324M, will not eliminate these low temperature reactions. The best way to minimize these reactions may be to use coals that have been extensively cleaned to remove the clays. Future studies will involve determining if these effects are also obtained with coal.
REFERENCES


Table 1. Results of quantitative analyses of 300°C 15 minute reactions.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>Additive</th>
<th>DBE</th>
<th>Tol</th>
<th>Total</th>
<th>Recovery (Wt %)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>86</td>
<td>4</td>
<td>90</td>
<td>95</td>
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<tr>
<td>2</td>
<td>Shell</td>
<td>-</td>
<td>0</td>
<td>27</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Shell</td>
<td>Pyrene</td>
<td>0</td>
<td>54</td>
<td>77</td>
<td>42</td>
</tr>
<tr>
<td>4</td>
<td>Shell</td>
<td>H6Py</td>
<td>1</td>
<td>61</td>
<td>83</td>
<td>72</td>
</tr>
</tbody>
</table>

* Based on weight % of DBE in feed.
** Based on weight % of pyrene or H6Py in feed. Recoveries include all pyrene species detectable by GC.

Table 2. Effects of feed/kaolinite ratio on product recovery.

<table>
<thead>
<tr>
<th>Feed/Kaolinite</th>
<th>Product Recovery*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2</td>
<td>7</td>
</tr>
<tr>
<td>4.9</td>
<td>7</td>
</tr>
<tr>
<td>15.6</td>
<td>17</td>
</tr>
<tr>
<td>38.5</td>
<td>87</td>
</tr>
</tbody>
</table>

* Based on weight % of DBE in feed.
INTRODUCTION

Previous work in this laboratory has investigated the hydrodesulfurization of Mequinenza (Spanish) lignite, a coal which is of interest for its remarkable organic sulfur content of about 11% on a dry basis. In experiments using impregnated molybdenum catalysts, sulfur removals of up to about 70% were obtained (1,2). In an ideal process configuration, the hydrodesulfurization reaction would remove the organic sulfur as H2S, leaving a sulfur-free or low-sulfur char suitable for combustion. However, it is inevitable that the reaction of a highly reactive lignite with hydrogen in the presence of a good hydrogenation catalyst will produce some liquids as by-products. In fact, in the experiment in which a sulfur reduction of 70% was achieved, 48% of the lignite was converted to liquid products, although most of the sulfur removed did appear as H2S. This behavior prompted an examination of the liquefaction reactivity of this lignite, with particular concern for the formation of liquids at relatively mild conditions and short reaction times.

Given's study of the liquefaction behavior of 104 high volatile bituminous coals included coal samples of up to 7.3% total sulfur (dry basis) (3). Examination of the data by cluster analysis showed that a factor representing sulfur had a major role in separating the coals into statistically separate groups. Subsequent work, using a set of 26 high volatile bituminous coals with a maximum sulfur content of 7.9% (dry basis), showed no significant relationships of the yields of oils, asphaltenes, or gas to sulfur content (4). The highest organic sulfur content of the coals used in that work was 3.3% (dry basis). The final comment in the 1988 paper (4) was that, "the role of sulphur in coals clearly merits further intensive study."

The work reported here used coals of different rank and much milder reaction conditions. Furthermore, a much smaller sample set was used. Therefore, our results are not intended to be a direct extrapolation of previous work (3,4), but rather represent a collateral line of investigation. The results presented here offer some insights into the exploitation of the relatively weak C-S bond for obtaining good liquids yields at mild conditions which might be typical of the low-temperature stage of a temperature-staged liquefaction system.

EXPERIMENTAL

Three lignites were used in this work: Hagel seam lignite from the United States, Cayhiran lignite from Turkey, and the Spanish Mequinenza lignite mentioned above. Some of the characteristics of these lignites are shown in Table 1. The principal criterion for the choice of these lignites was to obtain as wide a range of organic sulfur contents as possible. A secondary consideration, having first obtained the desired organic sulfur contents, was to obtain lignites with reasonably comparable carbon and hydrogen contents.

The procedure for conducting the reactions was the same regardless of the gas atmosphere or whether a catalyst was used. All reactions were carried out in microautoclave reactors (tubing bombs) of nominal 30 mL capacity. A 5 g lignite sample of dry lignite was used. No solvent was used in these experiments. The reactor was flushed three times with the desired gas, either nitrogen or hydrogen, before being pressurized to 6.9MPa. The pressurized reactor was then immersed in a sandbath preheated to 275°C. The reactor was subjected to vertical oscillation of 2.5 cm at 200 cycles/min for 30 min. At the end of an experiment the reactor was rapidly quenched by immersion in cold water.
The cooled reactor was vented into a glass expansion bulb from which samples could be withdrawn for gas chromatographic analysis. The reactor contents were washed with tetrahydrofuran (THF) into a dry Soxhlet thimble and were then extracted with THF for about 24 hr under nitrogen. The THF was removed from the extract by rotary evaporation. The solid residue was dried at 100°C for 18-20 hr before weighing. The gas yield was calculated by difference from the weights of the liquids and the THF-insolubles.

For experiments in which a catalyst was used, the lignites were impregnated with reagent grade ammonium tetrathiomolybdate, (NH₄)₂MoS₄. An amount of this salt sufficient to give a 1% molybdenum loading (expressed on a daf basis as elemental molybdenum, not the molybdate salt) was dissolved in sufficient distilled water to give a 1:1 lignite:water ratio. The lignite was slurried in the aqueous solution and stirred for at least 2 hr. Excess water was removed by vacuum freeze drying to a lignite moisture content below 1%. Typically the impregnation procedure was carried out with a large enough batch of lignite to suffice for a series of experiments. The dried, impregnated lignites were stored under nitrogen.

RESULTS AND DISCUSSION

An analysis of the yields of sulfur-containing liquids and H₂S, and of the selectivities to these products, as functions of conversion suggests that the net hydrodesulfurization process for the Mequinenza lignite occurs via a sequential mechanism which can be represented as

\[ S \text{ (lignite)} \rightarrow S \text{ (liquids)} \rightarrow H₂S \]

This analysis has been discussed previously (5) and is presented in detail elsewhere (6). Assuming that the reaction follows pseudo-first-order kinetics allows calculation of the apparent activation energy for hydrodesulfurization by the standard Arrhenius approach (e.g., 7). The apparent activation energy calculated in this way is 28.5 kcal/mole, which is in very good agreement with a value of 27.9 kcal/mole determined for the HDS of a coal-derived recycle solvent on a carbon-supported molybdenum catalyst (8). These results, particularly the indication of a sequential mechanism involving an initial production of liquids which are subsequently hydrotreated on the molybdenum catalyst, were the experimental basis for probing further into the first step - liquids formation - with particular interest in whether the unusually high concentration of organic sulfur in the Mequinenza lignite might have some effect on the liquefaction behavior.

The C-S bond is significantly weaker than the C-C bond. Although data in various reference sources vary slightly, values of 66 and 83 kcal/mole, respectively, are typical (9). These values were the basis for a hypothesis that a coal structure containing a high proportion of relatively weak C-S bonds may be more easily broken apart, relative to a structure with small concentration of C-S bonds, in either thermolysis or hydrogenolysis. To test this hypothesis the three lignites, with organic sulfur contents ranging from 0.8 to 11.35%, were reacted in both hydrogen and nitrogen atmospheres with and without a catalyst.

The relevant experimental results are summarized in Table 2. The results for reaction in hydrogen atmosphere show that the liquid yield increases as organic sulfur increases, regardless of whether the lignite was first impregnated with a catalyst. Similar results have been reported for other lignites (with the highest organic sulfur content being 6.0%), but that data was obtained at reaction temperatures of 380-460°C (10). The magnitudes of conversions and product yields in the experiments with catalyst and hydrogen gas are comparable to results obtained in the dry (i.e., without added solvent) catalytic liquefaction of a subbituminous coal at comparable reaction conditions (11). For reactions in nitrogen atmosphere, where presumably the decomposition of the coal structure would be due entirely to thermal effects, liquid yield also increased with organic sulfur for experiments in the absence of catalyst. This trend was not followed for reactions in nitrogen with the impregnated molybdenum catalyst, for reasons which are not clear. However, the Cayhiran lignite was the only one of the three to produce measurable quantities of H₂S during the reaction in nitrogen atmosphere, suggesting that the organic sulfur functional groups in this lignite might be different from those of the Hagel and Mequinenza lignites. The composition
of the gas produced in the treatment of the Cayhiran lignite was 77% CO₂ and 23% H₂S, suggesting that some of the sulfur functional groups in this lignite are readily susceptible to catalytic hydrogenolysis directly to H₂S, rather than breaking apart to form sulfur-containing liquids. For example, diaryl disulfides readily undergo reductive cleavage of the S-S bond to H₂S around 300°C (12).

For experiments in the absence of catalyst, both the Hagel and Cayhiran lignites showed an increase in liquid yield for reactions run in hydrogen relative to those run in nitrogen. In the case of the Mequinenza lignite, the liquid yields were essentially identical, within experimental error. This result suggests that the extensive array of C-S bonds enables a facile, thermally induced breakdown of the coal structure which is able to proceed without the intervention of hydrogen.

When reactions were carried out using lignites impregnated with the molybdenum catalyst, a greater yield of liquids was observed, from all three lignites, for experiments in hydrogen relative to those in nitrogen. Furthermore, the improvement in liquid yield, expressed as the difference between the yield in hydrogen and that in nitrogen, itself increased as a function of the organic sulfur content of the lignite. Thus for Hagel lignite the increased liquid yield in hydrogen was 0.7% (i.e., 3.0% in hydrogen vs. 2.3% in nitrogen), while for the Mequinenza lignite the increased yield in hydrogen was 4.5%.

We hypothesize that the key steps which facilitate the formation of liquids in high yield from the high organic sulfur lignites are the generation of thiols and the subsequent role of thiols in cleaving disulfide structures. The relative thermal instability of the S-S bond, which is even weaker (51 kcal/mole) than the C-S bond (13) is offered as an argument that disulfides should not be present in coals, because of the inability of the disulfide group to survive coalification (12). However, the lignites have not experienced extensive coalification. Thiols are easily formed, as for example, by hydrolytic cleavage of disulfides (14) or other organic sulfur functional groups. Once some thiols have been generated in the reaction, they can then facilitate the further reaction of disulfides. A mixture of disulfides and thiols will equilibrate (assuming no species are removed) to produce all possible reaction products; e.g.

\[ RSH + R'SSR' \rightarrow R'SH + R''SH + R'SSR' + RSSR + R''SSR + R''SSR + R''SSR \]

If steps are taken to prevent the complete equilibration of the mixture, then the reaction of the thiol with the disulfide can be exploited to achieve essentially permanent cleavage of the latter. In fact, such a disulfide cleavage by thiols is used in biochemical reactions, where such reagents as 2-mercapto-1-ethanol or dithiothreitol (Cleland's reagent) are used to cleave the disulfide linkage in proteins to the free thiol group in cysteine (15). Provided that the disulfide linkages in the lignites are bridging groups, rather than components of cyclic structures (a proviso analogous to the concept of open ethers and closed ethers among oxygen functional groups), the thiols formed by the initial reduction of some of the sulfur groups could then facilitate further depolymerization of the coal structure by reaction with the disulfides.

It has been suggested that organic sulfur is uniformly distributed throughout a coal sample, on the basis of solvent extraction work (16). Specifically, the sulfur content of extracts produced with various solvents is about the same from one solvent extract to another, indicating that even though individual solvents may be able to dissolve different portions, or extents, of the coal structure, approximately the same amount of sulfur is removed in each case. It is also recognized that in dry liquefaction a good dispersion of the catalyst is of special importance in obtaining good conversions (17). The dispersion of the catalyst obtained by the impregnation technique, combined with the inherent dispersion of the sulfur throughout the lignite structure, facilitate the initial reactions of the sulfur functional groups with hydrogen to generate thiols. Even though hydrogenolysis of the disulfide linkages may be continuing throughout the reaction, the cleavage of the disulfide linkage is further enhanced by the disulfide-thiol reaction.
ACKNOWLEDGEMENTS

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LITERATURE CITED

TABLE 1
Ultimate and sulfur forms analyses (dry, ash-free basis) of lignites used in this work.

<table>
<thead>
<tr>
<th></th>
<th>Hagel</th>
<th>Cayhiran</th>
<th>Mequinenza</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>71.34</td>
<td>68.15</td>
<td>64.81</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.50</td>
<td>5.50</td>
<td>5.72</td>
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<td>Nitrogen</td>
<td>1.14</td>
<td>2.21</td>
<td>0.96</td>
</tr>
<tr>
<td>Organic sulfur</td>
<td>0.79</td>
<td>4.91</td>
<td>11.32</td>
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<tr>
<td>Oxygen (difference)</td>
<td>22.23</td>
<td>19.23</td>
<td>17.19</td>
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Sulfur forms

<table>
<thead>
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<th>Hagel</th>
<th>Cayhiran</th>
<th>Mequinenza</th>
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<tbody>
<tr>
<td>Total sulfur</td>
<td>0.93</td>
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<td>12.64</td>
</tr>
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<td>Pyritic sulfur</td>
<td>0.10</td>
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<td>Sulfate sulfur</td>
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<td>Sulfide sulfur</td>
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<td>0.04</td>
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<tr>
<td>Organic sulfur</td>
<td>0.81</td>
<td>4.91</td>
<td>11.32</td>
</tr>
</tbody>
</table>

TABLE 2
Results of experiments in hydrogen and nitrogen atmospheres at 275°C, 6.9MPa gas pressure (cold) for 30 min.
Results are expressed on a dry, ash-free basis.

<table>
<thead>
<tr>
<th></th>
<th>Hagel</th>
<th>Cayhiran</th>
<th>Mequinenza</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂</td>
<td>N₂</td>
<td>H₂</td>
</tr>
<tr>
<td>Thermal (no catalyst)</td>
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<td></td>
<td></td>
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<tr>
<td>Total conversion</td>
<td>6.0</td>
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<tr>
<td>Liquid yield</td>
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<td>Gas yield</td>
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<td>Catalytic</td>
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<td>Total Conversion</td>
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<td>Gas yield</td>
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<td>3.2</td>
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TEMPERATURE PROGRAMMED AQUEOUS LIQUEFACTION EXTENDED TO SUPERCRITICAL CONDITIONS

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INTRODUCTION

Since coal contains highly diverse molecular structures with chemical bonds of various dissociation energies, the use of one single preselected reactor temperature to accomplish liquefaction is difficult to defend. Isothermal reactor conditions will likely result in the rapid rupture of weak bonds, a modest rate of cleavage of intermediate strength bonds, and probably leave the strong ones untouched. In attempts to address the chemical diversity within coals, the concepts of staged liquefaction and temperature programmed liquefaction have been devised (1-5) and the success of these efforts are encouraging.

Staged liquefaction is defined as using two or possibly more different temperatures over a specified time period to accomplish liquefaction. Temperature programming is defined as the raising of the reactor temperature through a defined sequence of temperatures over the liquefaction time period. In essence, the latter is staged liquefaction with up to an infinite number of temperature stages. The terminology for the latter is adapted from its common usage in chromatography.

The concept of temperature programming was developed as a technique to match the slurry medium's ability to donate hydrogen atoms with the rate of radical production from the coal. The specific objective is to prevent the newly formed coal radicals from undergoing retrograde dimerization reactions by allowing adequate time for the slurrying medium to donate hydrogens to them.

Temperature programming for liquefaction reactors using $\text{H}_2\text{O-H}_2\text{S}$ and Indian Head lignite in the subcritical temperature region, 300-350°C, gave higher yields than comparable ones using either 300°C or 350°C isothermal conditions (1,2). The temperature program profile was designed with the aid of thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (1-3,7,8).

The objective of this study is to extend the use of temperature programming of liquefaction reactions beyond the subcritical temperature region of the slurrying liquid, $\text{H}_2\text{O-H}_2\text{S}$ (1,2,9). ESR, TGA and DTA data are employed in the design of the temperature programs. The critical temperature of water in these reactors is approximately 374°C. However, since it is known to vary with the gaseous composition of mixtures.

EXPERIMENTAL

A 12-ml bath autoclave was used for these experiments (10). For all reactions, 1 g of as-mined Indian Head lignite (Zap, ND) ground to 200 mesh was charged along with 1 g $\text{H}_2\text{O}$, 0.117 g pyrrhotite ground to 200 mesh, 1.73 MPa $\text{H}_2\text{S}$, 3.39 MPa CO and 3.39 MPa $\text{H}_2$ into the autoclave. The heating block was preheated to the initial temperature, and the autoclave, when inserted into the heating block, reached 300°C 2.0 min. after insertion. Then, the heating block temperature was manually varied from 300 to the final temperature with the appropriate temperature program. After reaction, the products were washed with the desired solvent into a glass fiber soxhlet extraction thimble and extracted until constant weight was achieved. The yields were calculated using the mass of undissolved solid on the moisture- and ash-free basis. The proximate and ultimate analyses of Indian Head lignite are: moisture 29.5%, ash 9.0% moisture-free (mf), carbon 65.0% mf, hydrogen 4.2%, nitrogen 1.9% mf, sulfur 0.8% mg and oxygen 19.1% mf by difference.
RESULTS AND DISCUSSION

The rapid progression of temperature profiles (rapid profiles) employed herein are portrayed in Figure 1, and the slow progression of temperature profiles (slow profiles) used for this study are defined in Figure 2. The results obtained from using various temperature programs to liquefy Indian Head lignite are shown in Figures 3-9. Figure 1 illustrates the rapid profiles used to obtain the yield data of Figures 3-7 (points A through P). Figure 2 similarly portrays the slow profiles used to obtain the yield data of Figures 8 and 9 (points Q through T). Hereafter, when three percentage yields are given as the data from a given set of conditions, the three percentages refer to THF-, toluene-, and cyclohexane-solubility yields, respectively. The selection of the plateau temperatures of the temperature program used herein, 300°, 350°, 400° and 450° is discussed in the preceding article (2).

The isothermal data illustrated in Figure 3 and Table 1 serve as the baseline liquefaction yield data against with the yield data of the temperature programmed runs can be compared for relative effectiveness. When the residence time at 300°C is increased (programs A to D of Figure 1), the conversion to tetrahydrofuran (THF)-soluble products is enhanced (Figure 3).

When the liquefaction reactor temperature is isothermally kept at 350°C for 37.5 minutes, the conversions are improved by 22%, 23% and 11% (program G of Figure 1, Figure 4) from that of the 37.5-minute, 300°C isothermal reaction (program C of Figure 1, Figure 3). No appreciable further increases in the soluble product yields occurred by extending the residence time at 350°C from 37.5 to 60 minutes (programs G to H of Figure 1, Figure 4).

When the liquefaction reactor temperature is temperature programmed to proceed from 300 to 400°C over 60 minutes using the rapid profile (program L of Figure 1, Figure 5), the yields improved from that of the 350°C isothermal reaction (program H of Figure 1) by an additional 9%, 23% and 22%. When compared to the 400°C, 60-minute isothermal reaction, the 400°C programmed reaction gave yields which were improved by 9%, -14%, and 14%. When residence time at 400°C was increased from 0 to 40, minutes the cyclohexane-soluble product yields further improved (programs J to L of Figure 1, Figure 5) but the THF- and toluene-soluble product yields were essentially unchanged.

When the liquefaction reactor temperature was programmed to proceed from 300 to 450°C over 60 minutes using the rapid profile (program O of Figure 1, Figure 6), the product yields further increased from that of the 60-minute, 300 to 400°C program L by an additional 4%, 30%, and 9% (Figure 5). The residence time at 450°C (programs N to O of Figure 1) enhanced the toluene-soluble yield but had little effect on the THF- and cyclohexane-soluble product yields. The 300 to 450°C temperature programmed product yields at 37.5 minutes are +20%, -4%, and +8% changed from the yields obtained under comparable 450°C isothermal conditions (Table 1).

When the liquefaction reactor temperature is programmed from 300 to 480°C over 60 minutes using the rapid profile (program P of Figure 1, Figure 7), the cyclohexane-soluble product yield is enhanced and the THF-soluble product decreased from that of the 300-450°C reaction (program O of Figure 1, Figure 6). The 300-480°C, 60-minute programmed reaction provides 7% greater THF-soluble product yield than that of isothermal reaction of 480°C for 60 minutes (Table 1).

When the liquefaction reactor temperature is programmed from 300 to 350°C over 37.5 minutes using the slow profile (program Q of Figure 2, Figure 8), the product yields are 4%, 2%, and 1% increased from that of the comparable 350°C, 37.5-minute isothermal reaction (Figure 4). However, the differences are not statistically significant. At 60 minutes (programs Q to R of Figure 2), the corresponding yields are increased by 14%, 13%, and 6% from that of the related isothermal program H of Figure 1 (Figure 4).

When the liquefaction reactor temperature is temperature programmed to proceed from 300 to 400°C using the slow profile (program T of Figure 2, Figure 9), the yields are increased by 7%, 14%, and 4% from that of the comparable related rapid profile (program L of Figure 1, Figure 5) and 14%, 9%, and 20% from that of the 60-minute, 400°C isothermal reaction (Table 1). Residence time at 400°C was valuable in enhancing both the toluene- and cyclohexane-soluble yields (Figure 9).
In summary, the slow 300-400°C profile gives 95%, 83%, and 57%, the rapid 300-400°C profile gives 88%, 59%, and 53%, and the 400°C isothermal run produces 81%, 72% and 37% soluble product yields for the 60-minute reaction time.

CONCLUSIONS

Temperature programmed liquefaction gives superior yields compared to the corresponding isothermal counterpart and is dependent upon the nature of the temperature program profile. In a H2O/H2S medium using CO/H2/pyrrhotite/Indian Head coal over the 300-450°C temperature range, the use of two designed temperature program profiles is examined: one with a rapid progression of temperatures and a second with a slow progression. The liquefaction efficiency is measured by the yields of cyclohexane-, toluene-, and tetrahydrofuran-soluble products formed. The relative liquefaction yields for 60-minute reactions are: slow profile > rapid profile > isothermal. The rate of temperature progression through the three sequential 50-degree temperature segments influences the three yields differently. The residence time at 300°C is important in producing respectable yields of THF-soluble products, the 300-350°C temperature range further improves all three product yields, the 350 to 400°C temperature range primarily improves the yields of toluene- and cyclohexane-soluble products, and the 400-450°C temperature region further improves the toluene-soluble product yields. No special yield effects are observed on going from subcritical to supercritical aqueous conditions in the course of the temperature programs.

ACKNOWLEDGEMENT

We are grateful for the financial support of the United States Department of Energy.

REFERENCES


Table 1. Conversion Yields Using Isothermal Conditions

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Time, min</th>
<th>THF</th>
<th>Conversion yields, %a</th>
<th>Toluene</th>
<th>Cyclohexane</th>
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<tr>
<td>300</td>
<td>60</td>
<td>68</td>
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<td>350</td>
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<td>480</td>
<td>60</td>
<td>76</td>
<td>na</td>
<td>na</td>
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</tbody>
</table>

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Figure 1. Rapid temperature progression programs (rapid profile) used to liquefy Indian Head lignite.

Figure 2. Slow temperature progression programs (slow profile) used to liquefy Indian Head lignite.
Figure 3. The yields of soluble products obtained as a function of time isothermally at 300°C.

Figure 4. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 350°C.
Figure 5. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 400°C.

Figure 6. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 450°C.
Figure 7. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 480°C.

Figure 8. The yields of soluble products obtained as a function of time using the slow profile from 300 to 350°C.
Figure 9. The yields of soluble products obtained as a function of time using the slow profile from 300 to 400°C.
UNEXPLORED PRODUCTS FROM
REACTIONS OF LOW-RANK COAL IN AQUEOUS SYSTEMS

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Box 8213 University Station, Grand Forks ND 58201

INTRODUCTION

Processing of coal in aqueous systems has been investigated for a variety of purposes. The aqueous processing conditions can be divided into three temperature regimes. Temperatures over 375°C are considered to be liquefaction conditions. The liquefaction of coal in water and carbon monoxide at 400°C was demonstrated in 1921 by Fischer and Schrader (1). Appell applied aqueous processing to lignites and Bruceton coal in 1968 (2). An organic vehicle was also added in much of their study. Further development of aqueous carbon monoxide (CO-Steam) processing was conducted at the Grand Forks Energy Technology Center (3). Stenberg has reported the processing of low-rank coals in water-hydrogen sulfide mixtures (4). The chemistry of aqueous conversions of bituminous coals at 400°C has been investigated by Ross (5) and Ruether (6). Supercritical aqueous systems have also been investigated for low-rank coal liquefaction (7). Temperatures less than 300°C have been studied for coal activation in staged processing (8,9). Intermediate temperatures (300 to 370°C) are used in processes such as hot water drying of low-rank coals (10).

Our studies were directed toward elucidating the transformation of oxygen functional groups during processing of low rank coals. This paper reports the results from a matrix of reactions conducted in aqueous systems in the intermediate temperature range (300 to 325°C). The objectives were to determine the extent of conversion with an emphasis on decarboxylation and dehydration reactions under these mild conditions and to investigate the cleavage of oxygenated organic compounds, such as phenolics and ketones, from the coal structure. The effects of phase transfer catalysts in improving the conversion were studied. Also, the question of whether a submicron-particle-size dispersion of the coal in an alkaline medium has any effect on reactivity in the liquefaction was investigated.

In this intermediate temperature range, the changes in the coal were extensive enough so that conversion to soluble and volatile products was obtained, and detailed analyses of the products were carried out. The products were in some cases different from those obtained at higher temperatures. Some of these products are not stable at 375°C. In conducting experiments at the intermediate temperatures, there is less uncertainty about whether products resulted from primary or secondary reactions.

EXPERIMENTAL

A matrix of reactions were carried out under different conditions with a high sodium Beulah (ND) lignite (11). The lignite (850 micron size) was mixed with the aqueous medium in a 1:25 ratio. Reactions were carried out in a 300 ml Parr bomb reactor with magnetic stirring. The reactor was heated at the desired temperature (with cold charge) for one hour. At the end of the reaction period, the reactor was cooled to room temperature and the product
gases removed. The solid product was recovered by filtration. Percent conversion was reported as 100 minus the percent of the insoluble solid recovered (mf basis).

The basic filtrate was extracted with ether to give an ether-soluble extract of neutral components. Acidification of the filtrate and extraction with dichloromethane gave the base-soluble fraction (mainly phenolics and lactones). The physical and product yield data are given in Table 1. Along with various yield comparisons, the reaction products were examined with solid state $^{13}$C NMR, PAS-FTIR, and GC/FTIR/MS (12). Analyses of catechols were performed with an HPLC method.

One experiment involved testing a colloidal dispersion in aqueous 5% sodium hydroxide. The dispersions were made by blending the as-received coal with the aqueous base at high speed at ambient temperatures with a kitchen-style blender (11). These dispersions are very stable and are resistant to separation by centrifugation as well as filtration.

**RESULTS AND DISCUSSION**

The reaction of Beulah lignite in water (no reducing agent or catalyst) at 325°C was examined first as the basis for further investigations. Duplicate runs gave very low conversions (21%). The PAS-FTIR spectrum of the coal residue showed that some loss of carboxylic acids groups had occurred, and a small residual pressure of carbon dioxide was obtained as a result of the thermal decarboxylation. The $^{13}$C NMR spectrum of the residue showed it to be considerably deficient in aliphatic carbons in comparison with that of the unreacted Beulah. Analysis of the soluble products showed that the phenolic fraction consisted mainly of phenol and guaiacol, with smaller amounts of cresols and the series of methyl-, ethyl-, and propylguaiacol, and even smaller amounts of the other alkylphenols commonly found in coal pyrolysis products. This distribution of the phenolics, with the guaiacols in abundance, is unusual and therefore remarkable. Traces of catechols were also present. The portion of the coal structure which is most like lignin is evidently the most easily cleaved under neutral conditions. The neutral product fraction consisted mainly of cyclic ketones, such as substituted cyclpentanones and cyclopentenones, and small amounts of alcohols (13). These polar organic compounds were qualitatively analyzed with the GC/FTIR/MS.

Aqueous processing was next investigated by adding a mixture of formic acid and sodium formate to the suspension of coal in water and heating at 325°C for one hour. A significant increase (doubling) in the conversion was observed. A residual pressure of 200 psi was observed in the reactor after cooling. The gas contained CO$_2$ formed from the decomposition of formate, and CO$_2$ from decarboxylation and possibly the water gas shift reaction. FTIR spectroscopy of the unconverted residue confirmed the loss of carboxylic acid groups. The weight of soluble products was 75% of that predicted by the conversion data. In addition to the CO$_2$ from decarboxylation, water may be lost from the coal structure via dehydration reactions. The soluble products from the reaction were the phenolics and ketones. In this experiment with the added formate, the distribution of phenolics was more typical of low-rank coal pyrolysis or high temperature liquefaction product, with very small amounts of guaiacol and the alkyl-substituted guaiacols and large amounts of cresols and alkylphenols.
A similar liquefaction reaction was performed with the formate under basic conditions (5% aqueous NaOH). The conversion after heating at 325°C was about the same as that obtained in the formic acid/formate system above. Less decarboxylation was observed in this case. This finding is consistent with that observed at higher temperatures, that base retarded the decarboxylation, and acid conditions promoted the decarboxylation.

The phenolic products were typical of pyrolysis products with small amounts of guaiacols. Another class of compounds was found in significant amounts in these products from the alkaline reaction conditions. A series of lactones was observed in the material obtained by acidification of the base-soluble fraction. In the basic solution, the lactones are present in the hydroxy acid carboxylate form, which then closes up to the lactone during acidification. Four lactones were identified by matching mass spectra and infrared spectra (13). The identified lactones are γ-butyrolactone, α-methyl-γ-butyrolactone, γ-valerolactone, and γ-caprolactone. These lactones were absent in the previous experiments, which were run under neutral and acidic conditions.

A study of reactivity of colloidal dispersions of lignite was performed for comparison with the reactivity of the larger particle coal systems described above. The submicron dispersion of Beulah lignite in aqueous sodium hydroxide was prepared and heated with sodium formate at 325°C. The product yield data indicated that the conversion was roughly the same as that obtained from particulate coal suspensions in base under identical liquefaction conditions. It was concluded that conversion is dependent upon reaction temperatures, times, reducing agents, and catalysts and is independent of the particle size of the coal. This is probably because either the coal breaks down sufficiently or the reactions are not diffusion controlled.

The reaction of Beulah lignite at 325°C in aqueous sodium hydroxide, with no formate present, was also investigated. The conversion dropped considerably and was comparable to that obtained for the reaction in water with no reducing agent. Products were similar to those obtained in the alkaline formate reaction.

To study the effects of temperatures on conversion, decarboxylation and nature of products being formed, several reactions were carried out with the alkaline lignite dispersion with added formate at temperatures of 250 and 300°C. The conversions at 250°C were very poor (0 and 7%) and the conversion at 300°C (34%) was considerably lower than that obtained at 325°C. FTIR studies indicated that very little decarboxylation occurred at temperatures less than 300°C. Phenols were the major products as before.

Several possible coal structures may be considered as precursors for the lactone products obtained. The lactones were obtained under basic conditions even in the absence of formate; thus, a hydrolytic cleavage would seem to be more probable than a reductive cleavage. Hydrolysis of an ester linkage could liberate the γ-hydroxyacids at either the acid or alcohol end, or hydrolysis of a polyester could also give the hydroxyacids. Poly(γ-hydroxybutyric acids) are storage polymers of bacteria, and one could speculate on the incorporation of γ-hydroxyacids into coal structures as poly(γ-hydroxyacids), as a result of the same bacterial polymerase enzyme activity during the degradation of woody material. However, attempted acid hydrolyses of coals and treatment with methoxide at lower temperatures, which are normally appropriate for
transesterification, did not give the lactone or the transesterification product, the methyl ester of the hydroxyacid. In fact, no evidence exists for the presence of esters in the low-rank coals.

A more likely possibility is an ether hydrolysis, which would involve cleavage of a bond to the oxygen of the precursor to give the lactone or the hydroxyacid, as shown in Scheme 1. This could be initiated by attack of the carboxylate anion on one side of the ether linkage (substitution mechanism) or attack of base on groups on the other side of the ether linkage (elimination mechanism).

The origin of the cyclic ketones is also intriguing, and few clues are available for deducing the precursors. The most likely possibility is that an extensive thermal rearrangement liberates the ketone. An example of such a deep-seated transformation is the production of acetone during lignin pyrolysis at similar temperatures, where aromatic carbons are incorporated into the acetone structure.

The similarity between the γ-lactone products and the muconolactones involved in the fungal metabolism of alkylbenzoic acids and catechols derived from lignin may generate an opportunity to construct new models for coal structures and the coalification process. Further work is in progress to establish this theory.

REFERENCES
ACKNOWLEDGEMENTS

This research was supported by Contract No. DOE-FC21-86MC10637 from the U.S. Department of Energy. References herein to any specific commercial product by trade name or manufacturer does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof.
### TABLE 1

**REACTIONS OF BEULAH LIGNITE IN AQUEOUS SYSTEMS**

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Pressure (psi)</th>
<th>Catalyst</th>
<th>Conversion wt%</th>
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<td>NaOOCH</td>
<td>50</td>
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<td>none</td>
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<td>9.</td>
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</table>
SCHEME 1

1A

1B

1C
COMPARISON OF APPROACHES FOR MONITORING H-DONOR CONTENTS
UTILISING REPRESENTATIVE MODEL COMPOUNDS

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College Road, Stoke-on-Trent, Staffordshire. ST4 2DE. U.K.

ABSTRACT

The content of donatable hydrogen in hydrogenated samples of phenanthrene,
pyrene, fluorene, 1-methylnaphthalene and 2-methylnaphthalene have been calcu-
lated from $^{13}$Cnmr spectroscopy, gas chromatography and a chemical test using
sulphur as an hydrogen acceptor. Good agreement between the three approaches
was found for all the samples except hydrogenated fluorene where the value
from the sulphur approach was much higher. However, the ease of carrying out
the sulphur approach would suggest that it is a good method for monitoring the
donatable hydrogen content of process recycle solvents.

INTRODUCTION

As well as producing good conversions to low boiling point material, a coal
liquefaction process on present concepts needs to regenerate its own solvent
which should have a content of hydrogen donor compounds sufficient to maintain
effective dissolution of coal. In two stage liquefaction processes the solvent
is regenerated during the second stage where the coal liquid is catalytically
hydrocracked. Conditions must be set in this second stage to ensure that the
solvent fraction mass balance and its hydrogen content are maintained on recyc-
ling the solvent to the first dissolution stage. Consequently, monitoring the
amount and changes in composition of the recycle solvent is an important role in
liquefaction processes.

Since the recycle solvent fraction contains many different compounds, a detailed
assessment of changes in composition is difficult. However, an evaluation of the
'dissolving power' can be made if the hydrogen donor content of the recycle
solvent is measured. Several methods have been proposed for measuring the
hydrogen donor content with probably the most popular approach adopting quanti-
tative nmr spectroscopy. Amongst the other approaches, the use of hydrogen
acceptors in chemical tests have been suggested. For instance, Bockrath et al. used dibenzylmercury as a source of benzyl radicals to which hydroaromatic com-
pounds would donate hydrogen. Aiura et al. used sulphur as the hydrogen
acceptor and found good agreement with results calculated from nmr spectroscopy.

In this paper, a modified chemical test using sulphur is compared with quanti-
tative nmr for hydroaromatic mixtures produced by catalytic hydrogenation of the
parent aromatic compound; the donor content was also estimated from the gic anal-
ysis of the hydrogenated product. The aromatic compounds used were phenanthrene,
pyrene, 1-methylnaphthalene, 2-methylnaphthalene and fluorene whose hydroaromatic
derivatives have boiling points consistent with that of the recycle solvent.

EXPERIMENTAL

Hydrogenation of model aromatic compounds

All the hydrogenations were carried out in a 500ml capacity spinning/falling
basket autoclave manufactured by Baskerville Scientific Ltd and used a 15% Mo/
3% Co commercial catalyst supplied by Akzo Chemie, the Netherlands. Typically, 75g of the model compound were hydrogenated with 5.0g of catalyst at a feed pressure of hydrogen of 10MPa for 2h at 400°C.

Glc analysis of hydrogenated products

The products were analysed as %I% solutions in cyclohexane using a Perkin Elmer Sigma 3B Dual FID Chromatograph attached to a JJ Model GR 600 Pen Recorder and a LDC Model 300 Peak Area Integrator. 0.5 µl of the solution was injected through a pneumatic seal onto an OV 101, 25 m x 0.32 mm capillary column over a temperature program of 80°C initial temperature and 5°C min⁻¹ ramp rate. Identification of the peaks was assisted by gc/ms analysis, kindly carried out by British Coal, Coal Research Establishment.

Nmr spectroscopy analysis

Proton and 13Cnmr spectra were recorded on a Jeol Model PFT-90Q spectrometer fitted with a 10 mm probe. All solutions were made up in chloroform-d and TMS was added as an internal standard for the proton spectra; the chloroform-d peak at 76.99 p.p.m. was used as the standard for 13C spectra. To facilitate quantification of 13Cnmr, the paramagnetic relaxation agent, chromium acetylacetonate was added and 10,000 acquisitions were gathered at a 3s delay between the 90° pulses. A gated decoupling sequence was used during acquisitions.

Chemical testing of hydrogenated products with sulphur

0.2-0.3g (weighed to four decimal places on an analytical balance) was reacted with 0.5g of elemental sulphur in a 10ml capacity bomb-type autoclave (manufactured by Baskerville Scientific Ltd) fitted with a 0-10 bar Schaevitz pressure transducer linked to a digital readout. The bomb was maintained at temperature (250°C) until no further increase in the HzS pressure was observed. The measured pressure was related to the H-donor content using a calibration graph produced from similar experiments with known amounts of 9, 10 dihydrophenanthrene.

RESULTS AND DISCUSSION

Table 1 shows the contents of starting material, hydroaromatic, saturate and non-donor compounds for the hydrogenated products. Where the glc peaks could not be identified they were assigned to the non-donor heading. For phenanthrene the hydroaromatic content was 50% octa, 31% tetra and 3% dihydrophenanthrene with the remaining 16% being made up of butyltetralin, tetralin and the isomerisation compound cyclohexylmethyldian; of the non-donor compounds 14% was identified as biphenyl. The breakdown of the hydroaraynes was di, 25.5%; hexa, 57.9%; tetra, 5.4% and deca, 11.2%. The hydroaromatic content of the hydrogenated methylnaphthalenes contained both methyltetralins and tetralin and the non-donor compounds mainly consisted of decalin and naphthalene. For fluorene only 80% of the peaks were identified; the hydroaromatic content was all hexahydrofluorene and 49% of the non-donor material was diphenylmethane.

An estimation of the hydrogen donor content was made from glc using the integrated peak areas of the assigned peaks and multiplying by the number of donatable hydrogen. An example of the peak assignment is shown in figure 1 for hydrogenated pyrene. The values calculated are shown in table 2 as wt% donatable hydrogen product. The estimation of donatable hydrogen from 13Cnmr spectroscopy followed
the method of Clarke et al \cite{1} and the calculated results are shown in table 2 which also contains the values determined from the sulphur chemical test and values of aromaticities calculated directly from $^{13}$Cnmr spectroscopy; aromaticities were also calculated indirectly from proton nmr spectroscopy (following Brown and Ladner \cite{11}) and from gc analysis (denoted by the heading theoretical). A sample $^{13}$Cnmr spectrum for hydrogenated 1-methylnaphthalene is shown in figure 2 which clearly shows the aromatic and aliphatic regions separated by the peaks from the chloroform-d solvent.

Agreement between the three approaches is generally good, the S-method tending to produce the higher values and $^{13}$Cnmr the lower values. The donatable hydrogen content obtained from gc is compared with that from nmr in figure 3 and with that from the S-method in figure 4. It can be seen that for figure 3 the points tend to the left of the theoretical line and for figure 4 they tend to the right of the line.

The values for hydrogenated fluorene do show a wide variation compared with the other samples. The value obtained from gc could be an underestimate because of the relatively large proportion of the peaks that remained unidentified. Some of these peaks could have resulted from hydroaromatic compounds and might account for the difference between the gc and nmr spectroscopy methods but is not large enough to account for the difference to the value for the S-method. However, the product from the sulphur test did contain some black insoluble material, probably indicative of the occurrence of some polymerisation. Gc analysis of the soluble part of the product did show the formation of some higher boiling point material (retention time 1918s) and the disappearance of some of the lower boiling point material. Therefore, other reactions than dehydrogenation of hexahydrofluorene to fluorene occurred; these reactions may have produced gaseous alkanes which would contribute to the pressure rise. Unfortunately, analysis of the gas mixture after the reaction was not possible. Further experiments are now in hand to assess the other reactions occurring but the fact that these reactions occur even at 250°C (cf 600°C used for coal dissolution) may suggest that hydrofluorenes may not be good hydrogen donors.

CONCLUSIONS

Apart from the hydrogenated fluorene, the chemical test method using sulphur as an hydrogen acceptor has proved to be a good method for determining donatable hydrogen contents. The method requires only a small amount of sample, can be carried out in a few hours and used relatively inexpensive material. The gc approach would be unsuitable for recycle solvents because of the complex chromatograms and the difficulty in identifying all the peaks. The $^{13}$Cnmr approach needs more expensive equipment, a separate saturates determination and will take much longer in order to accumulate a good spectrum. The S-method has been tried with recycle solvents and has, to first estimations, shown good agreement with values calculated from $^{13}$Cnmr \cite{12}. The method is also more representative of the situation in coal dissolution in that it places the recycle solvent under hydrogen donation conditions.

ACKNOWLEDGEMENTS

The authors would like to thank the Science and Engineering Research Council and British Coal for their financial support and British Coal, Coal Research Establishment for carrying out and interpreting the gc/ion trap ms analysis.
REFERENCES

<table>
<thead>
<tr>
<th>STARTING COMPOUND</th>
<th>G.L.C. Analysis of Hydrogenated Product (wt%)</th>
</tr>
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<tr>
<td></td>
<td>Compound remaining</td>
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<tr>
<td>![Compound 1]</td>
<td>24.2</td>
</tr>
<tr>
<td>![Compound 2]</td>
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**Table 1. Analysis of the Hydrogenated Model Compounds**

<table>
<thead>
<tr>
<th>STARTING COMPOUND</th>
<th>DONATABLE HYDROGEN (2)</th>
<th>AROMATICITIES</th>
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<td>* S METHOD</td>
<td>G.L.C.</td>
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* CHEMICAL DEHYDROGENATION USING SULPHUR AS AN HYDROGEN ACCEPTOR

**Table 2. Donatable Hydrogen Content and Aromaticities of Hydrogenated Model Compounds**

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FIGURE 1 Gas-Liquid Chromatogram of Heterogenated Pyrene Showing Retention Times in Seconds

FIGURE 2 $^{13}$C NMR Spectra of Hydrogenated 1-Methylnaphthalene
FIGURE 3 Comparison of G.L.C. and $^{13}$Cnmr for the Determination of Donatable Hydrogen

FIGURE 4 Comparison of G.L.C. and S Method for the Determination of Donatable Hydrogen
AUTOCLAVE STUDIES INTO THE HYDROLIQUEFACTION OF COAL LIQUIDS:
THE EFFECT OF RECONTACTING THE CATALYSTS

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College Road, Stoke-on-Trent, Staffordshire. ST4 2DE. U.K.

ABSTRACT
Fresh and used catalysts (CoMo, NiMo, ZnMo and ZnW) were used in hydroliquefaction experiments with a Point of Ayr coal liquid over five contacts (2h, 400°C, 19MPa hydrogen) in spinning/falling basket autoclaves. For all catalysts conversions to low boiling point material, H:C ratios of distillation fractions, sulphur contents of the hydroliquefied liquids and carbon contents and specific surface areas of the catalysts were unaffected by repeat contact. However, the sulphur contents of the Mo-containing catalysts did increase with contact reflecting gradual sulphidation of the catalysts by the H₂S produced by desulphurisation of the coal feed; the sulphur content of the ZnW catalyst did not increase after the first contact.

INTRODUCTION
Aspects of coal liquefaction have been much researched, particularly with the re-emergence of interest caused by the oil crises in the 1970's. The types of reactors used in the studies have been various, ranging from small 'bomb' type microautoclaves through larger autoclaves and bench-scale continuous reactors to larger scale pilot or demonstration plants. The use of differently sized and designed high pressure equipment for liquefaction studies further complicates an already complex system and allows only limited comparison of results.

In a continuous reactor, particularly of the trickle bed type, intimate contact between the coal liquid and the catalyst will be maintained throughout the pass of the liquid feed. In an autoclave, particularly of the stirred design, the contact between the liquid and the catalyst will not be as intimate. The action of the stirrer will induce a centrifugal force which will tend to throw the liquid away from the catalyst surface. Consequently, it can be visualised that less strongly adsorbed molecules will spend a shorter time at the catalyst surface so that reaction rates and mechanisms could be very different from those observed in continuous reactor studies. In addition, steady state conditions can be readily investigated in a continuous reactor whereas, for a single contact in an autoclave, steady state conditions may not have been established and changes in catalyst activity will become more relevant.

EXPERIMENTAL
The coal liquid was one of two batches supplied by British Coal Research Establishment (CRE) and was produced by dissolving Point of Ayr coal in a process recycle solvent. The catalysts were prepared by the technique of incipient wetness using an alumina support supplied by Akzo Chemie, the Netherlands following a procedure described previously [1].

The hydroliquefaction experiments were carried out in spinning/falling basket autoclaves manufactured by Baskerville Scientific Instruments; a full
description of the autoclaves is given elsewhere. The experiments used 100g of the coal liquid and 4.0g of catalyst at a hydrogen pressure of 19MPa at a reaction temperature of 400°C for 2h. After the experiment the liquid product was transferred to a glass jar and stored under nitrogen; the catalyst was removed from the autoclave basket, rinsed with tetrachloroethane in an ultrasonic bath, air dried and stored in glass vials. In order to ensure that sufficient catalyst was available to take samples for analysis the following number of experiments were carried out for the five contacts: 1st contact, 5; 2nd contact, 5; 3rd contact, 4; 4th contact, 3; and 5th contact, 2 experiments making a total of 19 experiments per catalyst.

The hydrocracked product was separated into various boiling point fractions by vacuum distillation before analysis by gas chromatography using a Perkin Elmer Model Sigma 3B Chromatograph attached to a JJ Model CR 600 Pen Recorder and a LDC Model 300 Computing Integrator; 0.5 µl of a 1 wt% solution of the fraction in cyclohexane was injected onto a 25m x 0.32 mm OV 101 capillary column using a temperature program of initial temperature 80°C, ramp rate 5°C/min. The sulphur contents of the HL's for all the four catalysts are shown in figure 4, again indicate no dependence on repeat contact. The H:C ratios decreased with increasing bpt of the fraction. The sulphur contents of the HL's for all the four catalysts are shown in figure 5 with no dependence on repeat contact. The lower values for the two Zn catalysts only reflected the use of a different batch.
of CL whose sulphur content was less. In terms of the sulphur contents of the distillation fractions for NiMo and CoMo the average values, for the five contacts were 0.01, 0.02, 0.03 and 0.27% for the cold trap, the <250°C, the 250-275°C and 275-450°C fractions respectively, i.e. most of the sulphur in the recoverable material residing in the 275-450°C fraction which would represent the recycle solvent. There was very little change in the values with repeat contact showing that the solvent fraction will be recycled with a relatively high level of sulphur but that the sulphur concentration would not increase with recycle and the catalyst desulphurisation capacity would not be impaired. The level of sulphur in the recycle solvent is quite surprising bearing in mind the relative ease of desulphurisation compared with the denitrogenation or deoxygenation. Most, if not all, of the sulphur remaining will be in a ring in clusters and the likelihood is that some preferential adsorption on the catalyst surface has prevented some of the sulphur-containing molecules from reaching the catalyst surface.

The values for carbon contents and specific surface areas for the used ZnMo catalysts are shown in figure 6 and the sulphur contents of all the used catalysts are shown in figure 7. Only the sulphur contents of the catalysts showed any dependence on repeat contacts and the increase in sulphur content for Mo-containing catalysts indicated gradual sulphidation of the metal content of the catalysts. For the W-containing catalyst, ZnW, the sulphur contents remained relatively constant after the first contact, probably indicating that only the Zn content was sulphided and that the level of H₂S produced by desulphurisation was inadequate to cause sulphidation of the W content. Since it is accepted that presulphidation of Mo and W-containing catalysts enhances their activity, it might have been expected that catalyst activity would increase with contact because of sulphidation. However, it has been reported that 'in situ' sulphidation of catalysts does not lead to enhanced activity for autoclave studies, probably because of rapid carbon deposition, and hence increasing sulphidation with contact would be unlikely to enhance activity. In addition, it has been shown in further experiments with a presulphided CoMo catalyst that repeat contact did not affect conversion to low bpt material.

CONCLUSIONS

The investigation has shown that constant catalyst activity was attained after a single contact in the autoclaves. (Other work has shown that this situation also exists at longer reaction times and at different temperatures.) The conversions to low bpt material (hydrocracking), the H:C ratios (hydrogenation) and the carbon deposited on and the specific area of the catalysts (deactivation) as well as the contents of specific materials, e.g. phenanthrene and hydrophenanthrenes, were all unaffected by repeat contact in the autoclaves. Consequently, single contacts for hydroliquefaction investigations should be representative of steady state conditions. However, the results obtained from autoclave studies would not necessarily be reproduced in other types of reactors.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support provided by the Science and Engineering Research Council and British Coal Corporation and the supply of material by Akzo Chemie, the Netherlands and by British Coal Research Establishment.
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Figure 1. Variation of amounts of fractions with repeat contact with CoMo.

Figure 2. Variation of amounts of fractions with repeat contact – average values for all catalysts.
Figure 3. Variation in amounts of hydrophenanthrenes (1st bar), phenanthrene (2nd bar) and material bpt < naphthalene (3rd bar) with repeat contact. HL = hydrocracked liquid; 0 contact indicate coal liquid feed.

Figure 4. Variation of H/C ratio of distillation fractions with repeat contact. For each contact: 1st bar = cold trap; 2nd bar = <250°C; 3rd bar = 250-275°C; 4th bar = 275-450°C
Figure 5. Variation of sulphur content of hydrocracked liquid (HL) with repeat contact.
For each contact: 1st bar - CoMo; 2nd bar - NiMo; 3rd bar - ZnMo; 4th bar - ZnW.

Figure 6. Variation of sulphur content and specific area of catalysts with repeat contact.
Figure 7. Variation of sulphur content of catalysts with repeat contact.
TRATE ELEMENT REDUCTION IN FILTERED COAL EXTRACT SOLUTIONS USING SOLVENT PRECIPITATION

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Department of Chemical Engineering, University of Nottingham, Nottingham, NG7 2RD, UK.

INTRODUCTION

In two-stage coal liquefaction processes the coal is digested in a solvent in the first stage and then hydrocracked in the second stage in order to increase the hydrogen to carbon ratio and the yield of distillate material. At some point in the process mineral matter and undissolved residual material must be removed, and the processes used for this step are usually filtration or solvent deashing, with the latter taking the form of anti-solvent or critical solvent deashing. The deashing step can occur either between the first and second stages or after the second stage. The major advantage of deasing before the second stage is that it reduces catalyst deactivation during hydrocracking due to both carbon deposition and trace element deposition as reported by Stohl and Stephens. However, even when deashing occurs before the second stage, deactivation of the catalyst still occurs due to both carbon and trace element deposition. In the case of carbon deposition the cause is not known, although there is some evidence linking high molecular weight species to carbon deposition. With trace elements none of the deashing processes in use is completely effective and, therefore, some trace elements go forward to the hydrocracking stage.

The British Coal process is a two-stage process with filtration as the deashing step occurring between the digestion and hydrocracking stages. Previous work in this laboratory using Point of Ayr and Calverton coals has shown that increasing the digestion pressure considerably reduces the ash level in the extract solution after filtration, and that where this effect is modified by the use of different coals or hydrogen-donating solutions, then this can be overcome by reducing the filtration temperature. It was also shown that the distribution of trace elements in the original coal ash was different from that in the extract solution ash. For example, the proportions of manganese and titanium increased twenty-fold and ten-fold respectively, and the proportions of calcium and magnesium also increased. These elements, which show an increase in proportion, have also been found to be catalyst deactivators and were also found to deposit most readily on the hydrocracking catalyst. Thus, it is important that the level of these trace elements is as low as possible if their deposition on the hydrocracking catalyst is to be reduced.

Previous work studying the form of the trace elements remaining in the filtered coal extract solution shows that their removal is no easy matter. They pass through fine filters and are
not easily removed by guard beds \(^{19}\). Increasing the digestion pressure, as described above, has been successful, but efforts to reproduce this effect at low digestion pressures, by the addition of low-boiling material prior to filtration, were unsuccessful \(^{10}\). However, it has been shown \(^{10}\) that the insoluble portion of solvent extractions, used to characterise the filtered coal extract solution, contain a high proportion of the trace elements present in the original extract. The solvents used were pentane, toluene and THF, and with toluene, for example, about 80% of the trace element content precipitated out with the insolubles. Thus, it may be possible to carry out a solvent precipitation on coal extract solution which has already been filtered, in order to reduce the trace element concentration to a very low level.

In this paper work carried out using toluene and THF to remove trace elements from filtered coal extract solutions will be described. The effect of extract to solvent ratio was studied as well as the temperature of extraction. Trace element concentrations have been measured both before and after precipitation, and the nature of the extract solution after solvent precipitation, compared to that of the original extract solution, has been examined.

EXPERIMENTAL

Materials

The coal used was Point of Ayr, supplied by British Coal, preground to -200 mesh. An analysis of the coal is given in Table I. The solvent used in the digestion was process-derived hydrogenated anthracene oil (HAD), again supplied by British Coal.

Procedures

Liquefaction was carried out by heating a mixture of the coal and HAD to a temperature of 400-420°C in a 2 litre autoclave. The pressure was controlled by venting vapours, as required, to a condensing trap. At the end of the digestion period, which was 45 minutes above 400°C, the contents were cooled to the filtration temperature and vapours vented to reduce the pressure to the filtration pressure. The mixture in the autoclave was then filtered through a pressure filter containing a "Nomex" cloth using the residual pressure in the autoclave. A solvent-to-coal ratio of 2:1 was used. The procedure has been described previously \(^{9}\).

Solvent precipitation experiments were carried out on the filtered extract solution, produced as described above, using a stirred 0.2 litre autoclave. The extract and solvent were mixed together cold, in the autoclave, and then heated to the extraction temperature in a fluidised sand bath. The mixture was agitated at the extraction temperature for 20 minutes and then filtered, using the pressure in the autoclave or an applied nitrogen pressure, into a pressure filter containing a "Nomex" cloth at the extraction temperature. Some experiments were also carried out where the solvent was injected, using an applied nitrogen pressure, into the autoclave.
containing the extract at the required temperature.

**Analysis**

Ash yields of the liquid products were determined by evaporating a sample (±25 g) in a platinum crucible until coke formed. The ashing was completed in a muffle furnace set at 850°C.

Trace element analysis was carried out on the ash by carrying out a fusion with lithium metaborate followed by dissolution in 10% hydrochloric acid. The resulting solution was analysed using atomic emission and absorption spectrometry (AA). The method has been described previously.²

Analysis was carried out on the fractions which boiled below 350°C of the extract and the filtrate produced after solvent precipitation, using a Perkin Elmer model 8500 GC fitted with a wide-bore, OV-1 capillary column 25 m long and 0.53 μm diameter. The oven temperature was 40°C for 1 minute followed by a temperature ramp at 4°C per minute to 250°C where the temperature was held. Carrier gas was helium at a flow of 6 cm³/min. There was no split on the sample injected into the column and a FID detector was used. Initial fractionation of the samples was carried out by vacuum distillation.

**RESULTS AND DISCUSSION**

**Reduction in ash levels**

In the first series of experiments toluene was used as the solvent and the extractions were carried out at a temperature of 110°C. The ratio of extract to toluene was varied and a blank run was also carried out with no toluene added. This was to make certain that no precipitation was occurring as a result of cooling and reheating the filtered extract solution. These results are shown in Table 2.

From the results in Table 2 it can be seen that by increasing the quantity of toluene used then the amount of material precipitated is increased and the ash level of the filtrate decreases. It is clear, from the filtrate mass, that there is still a significant quantity of toluene remaining. At the temperature used this might be expected. To allow for this an equivalent extract ash is calculated as shown in Table 2. This figure also shows a steady decrease as the mass of toluene used increases. The mass of cake obtained shows that there would be a significant loss of product, by precipitation, if this method were to be used to remove trace elements. The extract solution used in this series of experiments had a "high" ash value of 0.036%. In the next set of experiments an extract solution with a lower ash value of 0.016% was used and the effect of varying the extract temperature was studied.

Table 3 shows that as the temperature of extraction is increased, then the mass of cake decreases, but the equivalent extract ash increases. However, it would seem that a significant reduction in the amount of material precipitated can be obtained without a large
increase in the ash level of the filtrate. This is especially seen in the increase in temperature from 100 to 138°C.

All the above experiments were carried out by mixing the extract and toluene together cold in the autoclave and then heating to the extraction temperature. In a commercial operation, the solvent would probably be added to a hot extract. This was simulated by injecting toluene into heated extract at the required temperature. The results obtained were similar to those shown in Tables 2 and 3.

Table 4 shows the results obtained when THF is used as the solvent. The reason THF was tried was that the normal value of the THF insolubles is about 2-4%, but it was noted that over 60% of the trace elements precipitated out with the insolubles. Thus, it may be possible to reduce the trace element concentration with only a small amount of material precipitated. However, the results obtained from these experiments show that THF gave little, if any, reduction in ash level in the extract solution.

The results for toluene show that it is possible to reduce the trace element concentration in filtered extract solutions using this method. There is a price to pay, however, and that is loss of product as precipitated material. This can be reduced by increasing the extraction temperature to an optimum level. However, the value of this lost product is questionable, since it will be mainly preasphaltenic, difficult to convert to useful products in the hydrocracking stage and could be responsible for much of the carbon deposition on the hydrocracking catalyst.

Trace element concentrations

Not only is the overall ash level important in the coal extract solution, which is fed to the hydrocracking stage, but also the concentration of the individual trace elements. Table 5 shows the concentration of trace elements in the ash from the original extract and the filtrate produced after toluene extraction. This was for an extract with an ash level of 0.035%, extracted with toluene at 165°C to give a filtrate with an ash level of 0.01%. The results show that there are some differences, with calcium reducing and iron and titanium increasing their proportions. However, the changes are not great and it would be expected that if the filtrate were fed to the hydrocracker it would deposit trace elements as observed previously, except, of course, there would be a smaller quantity overall.

Nature of the extract solution after precipitation

When toluene extractions were carried out at 110°C it was clear that toluene remained in the filtrate from the mass obtained. With the higher temperature extractions the filtration was also carried out at the same temperature and the mass of filtrate was accordingly lower as most of the toluene was boiled off from the filtrate. However, examination of the filtrate showed that it was much more fluid than the original extract and it appeared that some toluene remained in it. Analysis of the extract and filtrate were
carried out using an initial vacuum distillation and GC analysis as described previously. The aim being to find how much toluene remained. However, no toluene was seen in the chromatogram.

Table 6 shows some results obtained for the simulated distillation of extract and filtrate after toluene extraction. It can be seen that the fraction boiling up to 150°C is reduced after extraction, contrary to expectations, and that the fraction from 200-300°C increases, mainly in the 250-300°C range. Examination of the chromatogram shows no difference in the actual components present, only differences in their quantity. With the low boiling material the reduction is probably a consequence of the heating at elevated temperatures during filtration coupled with the stripping of the toluene. The reason for the increase in the other ranges is not known and more extensive analysis is required to answer this problem.

ACKNOWLEDGEMENTS

This work was funded as part of a grant from the Science and Engineering Research Council, UK. The assistance of British Coal, Coal Research Establishment and Liquefaction Project, is gratefully acknowledged in their supply of materials and useful information.
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Table 1  Analysis of Point of Ayr Coal

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<th>Proximate analysis</th>
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</table>

Table 2  Extraction of coal extract solution with toluene - effect of toluene to extract ratio

Temperature of extraction : 110°C
Ash of original coal extract solution : 0.056%

<table>
<thead>
<tr>
<th>Mass Extract (g)</th>
<th>Mass Toluene (g)</th>
<th>Ratio Extract/Tol</th>
<th>Filtrate - Mass (g)</th>
<th>Ash (%)</th>
<th>Cake - Mass (g)</th>
<th>Ash (%)</th>
<th>Equivalent Extract Ash (%)</th>
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Note: Equivalent Extract Ash = \( \frac{\text{Mass of Filtrate} \times \text{Filtrate Ash}}{\text{Mass Extract}} \)

Table 3  Extraction of coal extract solution with toluene - effect of temperature

Ratio extract/toluene : 1.67:1
Ash of original coal extract solution : 0.018%

<table>
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Note: Equivalent Extract Ash = \( \frac{\text{Mass of Filtrate} \times \text{Filtrate Ash}}{\text{Mass Extract}} \)
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<td>1.67:1</td>
<td>1.67:1</td>
<td>1.67:1</td>
<td>1:1</td>
</tr>
<tr>
<td>Filtrate Mass (g)</td>
<td>55.1</td>
<td>59.3</td>
<td>46.6</td>
<td>41.5</td>
</tr>
<tr>
<td>- Ash (%)</td>
<td>0.012</td>
<td>0.013</td>
<td>0.016</td>
<td>0.011</td>
</tr>
<tr>
<td>Cake Mass (g)</td>
<td>4.1</td>
<td>4.8</td>
<td>4.8</td>
<td>9.5</td>
</tr>
<tr>
<td>Extract Ash (%)</td>
<td>0.013</td>
<td>0.015</td>
<td>0.022</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Table 5 Trace element analysis

<table>
<thead>
<tr>
<th>Element in Ash (%)</th>
<th>Original Extract</th>
<th>Filtrate after Toluene extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>5.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Ti</td>
<td>1.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Si</td>
<td>4.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Ca</td>
<td>25.6</td>
<td>15.2</td>
</tr>
<tr>
<td>Mn</td>
<td>3.0</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe</td>
<td>3.8</td>
<td>8.2</td>
</tr>
<tr>
<td>Mg</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>Na</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>K</td>
<td>0.5</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6 Simulated distillation of extract and filtrate after extraction with toluene at 165°C

<table>
<thead>
<tr>
<th>Original Extract (%)</th>
<th>Filtrate 1 (%)</th>
<th>Filtrate 2 (%)</th>
<th>Filtrate 3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-100°C 0.47</td>
<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>0-150°C 1.21</td>
<td>0.10</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>0-200°C 6.97</td>
<td>5.11</td>
<td>4.28</td>
<td>4.18</td>
</tr>
<tr>
<td>0-250°C 19.3</td>
<td>32.9</td>
<td>20.0</td>
<td>21.1</td>
</tr>
<tr>
<td>0-300°C 54.6</td>
<td>78.5</td>
<td>64.1</td>
<td>67.5</td>
</tr>
<tr>
<td>0-350°C 100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Extracts prepared with an extract:toluene ratio of:
1: 1.6:1
2: 2.5:1
3: 3.3:1
Fig. 1. A comparison of the plastometry curves for coal H1 at 0.5 and 5 MPa (Heating Rate 3 °C min⁻¹)
Fig. 2. The variation of plastometry torque parameters with pressure for Coal H1 (Heating Rate 3°C min⁻¹)
Fig. 3. The variation of plastometry torque parameters with heating rate for coal H1 (Pressure 2 MPa)

Fig. 4. The effect of heating rate on the dilatation of coal Oa (Gauge pressure - 2 MPa)
Fig. 5. The variation of dilatation with plastometry torque parameters at 2 MPa pressure for coal Oa.

Fig. 6. The variation of optical anisotropy index (OAI) with heating rate for coal Oa (Pressure 2 MPa).
ACTIVITY AND CHARACTERIZATION OF COPROCESSING CATALYSTS PRODUCED FROM AN IRON PENTACARBONYL PRECURSOR

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ABSTRACT

It is generally believed that highly dispersed catalysts are very effective in the conversion of coal to liquids, but the effects of dispersion and composition have not been adequately investigated. We chose to study the use of iron pentacarbonyl, Fe(CO),, to produce a highly dispersed catalyst in situ in the coprocessing of Illinois #6 coal and Maya ATB residuum. The activity of the catalyst produced from this precursor has been investigated, and its particle size and composition measured using X-ray diffraction, Mössbauer spectroscopy, and transmission electron microscopy (TEM). Use of 0.5 wt% Fe added as Fe(CO), resulted in an increase in coal conversion to methylene chloride solubles from 39% to 82%. The Fe(CO), precursor decomposed in the reactor to produce a mixture of highly dispersed pyrrhotite, (Fe,,S), Fe,C, and other iron compounds. However, with time at reaction conditions, 95% of the iron was converted to Fe,_,S. The pyrrhotite particles formed in the initial stages of reaction had a mean crystallite size of 12 nm when measured using X-ray diffraction line broadening; the small particle sizes were confirmed by TEM and Mössbauer studies.

INTRODUCTION

Coprocessing is the liquefaction of coal in a heavy petroleum medium such as a heavy crude or residuum. Conventional direct liquefaction processes must recycle two-thirds of the coal-derived oil, but coprocessing can operate completely or largely in a "once through" mode, eliminating the cost and complication of the large recycle. (1) In addition, metallic impurities in the oil deposit on the coal residue or pitch.

In most direct coal liquefaction processes, the use of catalysts results in more desirable products under less severe processing conditions. The same is true for coprocessing, which may require even more effective catalysts because the petroleum-derived slurrying oils used in coprocessing are often poor hydrogen donors. In direct coal liquefaction, supported metal catalysts (e.g. CoMo/Al,O,) may suffer from poor contact between the coal and the catalyst. Unsupported dispersed catalysts can offer good contact between the coal and the catalyst. As early as 1924 it was known that the addition of iron sulfides to the liquefaction mixture would improve yields. (2) Addition of low surface area solids requires high catalyst concentrations. Particulate pyrite addition has been studied and found effective in concentrations of 10wt%. (3) One method of increasing dispersion (surface area per mass) is to introduce the catalyst as a soluble precursor. Such precursors are distributed throughout the coal-oil mixture by
dissolving in the oil, and they decompose upon heating or other treatment to form very small catalyst particles within the coal-oil mixture. The high dispersion allows catalyst concentrations of less than 1.0wt% to be used. Examples of these catalyst precursors are nickel acetate, (4) carboxylic salts of iron or molybdenum, (5) water-soluble ammonium molybdate, (6) molybdenum naphthenate (7), and carbonyl compounds of iron, molybdenum, and other metals. (8) Crystallite sizes as low as 15-30nm have been reported for a Ni acetate precursor. (4)

Several studies have reported the use of Fe(CO)$_6$ and other iron carbonyls in direct liquefaction in a hydrogen-donating solvent. (9-12) These studies showed that the Fe(CO)$_6$ precursor produced a catalyst active for hydroliquefaction of coal using Fe at 2.0wt% of the feed coal. The precursor was converted to a less active iron oxide (Fe$_3$O$_4$) in the absence of added sulfur, but when sulfur was added in the form of elemental sulfur or organic sulfur compounds, the more active iron pyrrhotite (Fe$_{1-x}$S) was formed. (10) Increases in coal conversion were found with both bituminous and subbituminous coals. (11) The use of other soluble precursors such as cyclopentadienyliron dicarbonyl dimer, (C$_5$H$_5$)$_2$Fe$_2$(CO)$_4$, yielded increased coal conversions of the same order of magnitude as Fe(CO)$_6$. (8) However, particle sizes of liquefaction catalysts produced from the decomposition of Fe(CO)$_6$ have not been reported in the literature, but other studies have shown that iron particles less than 10nm in diameter can be deposited on carbon or zeolite supports by thermal decomposition. (12,13)

**EXPERIMENTAL**

Illinois #6 (Burning Star) hvB bituminous coal ground to -200 mesh (<74µm) was obtained from the Pittsburgh Energy Technology Center and used as received. Maya ATB (650°F+) residuum was obtained from Citgo. Analysis of the coal is shown in Table 1. The Maya ATB had a composition of 85.9%C, 10.2%H, 0.5%N, and 4.8%S, with a Conradson Carbon residue of 15.2%. Iron pentacarbonyl was obtained from Strem Chemical and filtered through glass wool when necessary to remove iron particles produced by decomposition of the carbonyl.

<table>
<thead>
<tr>
<th>Table 1. Ultimate and Proximate Analyses of Illinois #6 Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
</tr>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>Sulfur</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Oxygen (diff.)</td>
</tr>
</tbody>
</table>

Ultimate analysis is on a dry basis
Analyses performed by BCR National Laboratory

Coprocessing experiments were conducted in a 300ml stainless steel autoclave (Autoclave Engineers) agitated by a turbine impeller and heated by a tube furnace. Coal (12.5g, as rec.), 37.5g Maya ATB residuum, and from 0-8.8g (0-5wt%Fe) catalyst precursor were placed into the reactor, which was flushed with helium and stirred at 50°C for two hours.
to ensure mixing of the precursor in the viscous residuum. The reactor was pressurized with hydrogen to 6.9 MPa, heated to 425°C in approximately 40 minutes, and held at 425°C for 60 minutes while stirring at 1300 rpm. The reactor was then cooled to below 300°C in about five minutes. Conversion was determined using Soxhlet extraction with methylene chloride. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles were determined by adding 40 volumes of n-pentane to the methylene chloride (CH₂Cl₂) solubles, and using Soxhlet extraction with pentane.

A Phillips X-ray Diffractometer using Cu-Kα radiation at 30kV and 20mA was used to obtain powder diffraction patterns of the catalysts. The Scherrer equation was used to calculate average crystallite sizes from line broadening of the peaks, corrected for instrumental broadening. (14) Mössbauer spectroscopy was performed using a 100 mCi source at both room temperature (290K) and cryogenic temperatures (10K, 80K). Transmission electron microscopy was carried out using a JEOL 2000FX STEM (100kV beam) with an energy dispersive X-ray spectrometer. A Bruker MSL 300 FT-nuclear magnetic resonance spectrometer was used to obtain the carbon aromaticity (fₐ) of soluble coprocessing products.

RESULTS AND DISCUSSION

Coprocessing of Illinois #6 coal with Maya ATB was carried out with varying amounts of Fe(CO)₅ precursor. The conversion to methylene chloride solubles increased rapidly as the catalyst concentration was raised from 0 to 0.5 wt% Fe (based on the total coal + residuum feed), but increased much more slowly from 0.5 to 5wt% Fe (Figure 1). The use of only 0.2 wt% Fe was sufficient to increase conversion to 65%, vs. 39% for the no-catalyst case. The fact that an amount of iron considerably less than that already present in the coal can produce such an increase shows the benefit of using a precursor which will give high dispersion.

The effect of the iron catalyst produced from the precursor appears to be limited to conversion of the coal rather than hydrogenation of the residuum or subsequent upgrading of the coal liquids produced. Catalyst addition produced little change in the asphaltene fraction of the product (it increased from 12% of the product to 15%). Table 2 shows that the H/C ratio of the products does not change significantly with catalyst addition, and heteroatoms are not removed to any appreciable extent. The aromaticity (fₐ) of the CH₂Cl₂ solubles does increase with catalyst addition due to the high aromaticity of the additional liquids produced from the coal.

Table 2. Analyses of CH₂Cl₂ Solubles from Coprocessing using a Fe(CO)₅ Catalyst Precursor

<table>
<thead>
<tr>
<th>Fe(CO)₅ (wt% Fe)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>H/C(atomic)</th>
<th>fₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>83.3</td>
<td>10.5</td>
<td>0.2</td>
<td>2.6</td>
<td>1.49</td>
<td>0.36*</td>
</tr>
<tr>
<td>2.5</td>
<td>83.1</td>
<td>10.6</td>
<td>n.d.</td>
<td>2.6</td>
<td>1.53</td>
<td>0.40</td>
</tr>
<tr>
<td>5.0</td>
<td>84.0</td>
<td>10.6</td>
<td>0.3</td>
<td>2.4</td>
<td>1.51</td>
<td>---</td>
</tr>
</tbody>
</table>

*fa of Maya ATB is 0.33

XRD and Mössbauer spectroscopy were used to determine the composition and
dispersion of the catalysts produced from Fe(CO)$_3$. The results are presented in Table 3. The properties of the catalyst at various stages of reaction were of interest, so a number of samples of insoluble coprocessing residue were analyzed. The first sample (referred to as 425°C - 0 min.) was prepared by heating a mixture of coal, residuum, and Fe(CO)$_3$ (2.5 wt% Fe) to the reaction temperature of 425°C, then cooling the mixture immediately. This sample represents the condition of the catalyst before extensive coal conversion has taken place. X-ray diffraction patterns of this sample showed a fully developed pyrrhotite pattern. This result agrees with the results of Suzuki et al. (10), and should be expected since the Maya residuum is high in sulfur (4.84 wt%). A line broadening calculation on the largest pyrrhotite peak gave an average crystallite diameter of 12.0nm.

The second sample (425°C - 60 min.) consisted of the insoluble residue which remained after reaction of coal, residuum, and Fe(CO)$_3$ for 60 minutes at 425°C. This sample represented the state of the catalyst after it had spent a longer time under the reaction conditions. This sample also showed a pyrrhotite pattern, but with an average crystallite diameter of 20.5nm. The increase in crystallite size is likely due to the sintering of small metal catalyst particles which commonly occurs at elevated temperatures. (15) Djega-Mariadassou et al. found that when iron oxide aerosols (~80nm) were used as liquefaction catalysts, the small particles were very sensitive to sintering, but in the presence of coal the effect was inhibited. (16) This was attributed to the coal depositing heavy organic residues on the surface of the catalyst.

In order to distinguish the iron added as Fe(CO)$_3$ from the iron originally present in the coal, XRD and Mössbauer spectroscopy were performed on a sample of Illinois #6 coal and on a coprocessing residue to which no catalyst had been added. Table 3 shows that the coal exhibited only a weak diffraction pattern for FeS$_8$, and that the coprocessing sample without added Fe(CO)$_3$ gave a weak Fe$_3$S$_2$ pattern. Since these patterns were weak compared to the samples with added catalyst, it was concluded that the XRD signal was mostly due to the added catalyst.

Mössbauer spectroscopy confirmed the presence of the pyrrhotite detected by XRD, but revealed some other species which were, perhaps because of their small particle size or lack of crystallinity, invisible to XRD. The 425°C - 0min. sample was found to consist of only 26% pyrrhotite, with about an equal amount of iron carbide and almost 50% of iron oxide/oxyhydroxide. The oxide/oxyhydroxide may have been produced in the reaction, or it may have been originally α-Fe which was oxidized when the sample was exposed to air. In any case, it is interesting to see that the precursor may form a variety of iron compounds in the reactor. The source of the iron carbide is probably Fe(CO)$_3$ and not the pyrite originally in the coal, since the transformation of pyrite to iron carbide is thermodynamically unfavorable under these conditions. Condition and Cashion have also observed the formation of iron carbide from Fe$_3$(CO)$_12$ when they used it as a catalyst precursor in the liquefaction of a brown coal. (17) Mössbauer analysis of the 425°C - 60 min. sample showed that after 60 minutes at the reaction conditions, most of these intermediates had been transformed to pyrrhotite, with a small amount of iron oxide remaining. In the high-sulfur environment of the coprocessing reaction, it is thermodynamically favorable for all of the iron to be converted to pyrrhotite.

The Mössbauer results show that the pyrrhotite was not the common mineralogical type, monoclinic Fe$_2$S$_9$, but was a somewhat poorly formed intermediate variety. In addition to the composition, the Mössbauer spectra provided information as to the size of the catalyst particles. There was a significant difference between the room temperature spectrum and those obtained at cryogenic temperatures, indicating the presence of superparamagnetic iron-bearing particles, which only occurs when particles are on the order of 20nm or less. (18) Transmission electron microscopy was employed to independently verify the size range of the iron-containing particles produced from the Fe(CO)$_3$ precursor. To eliminate interference of the iron and other mineral matter in the coal, a model catalyst system was used which consisted of activated carbon with iron deposited on it. The model catalyst was produced by heating a mixture of activated carbon (with a very low iron content), toluene
Table 3. X-ray Diffraction and $^{57}\text{Fe-Mössbauer}$ Data for Products of Fe(CO)$_5$ Decomposition

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{57}\text{Fe Mössbauer Phases (%iron)}$</th>
<th>XRD - Iron Phases Identified (mean diam.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coprocessing Residue Fe$_{1-x}$S (26%)</td>
<td>Fe$_{1-x}$S (26%)</td>
<td>Fe$_{1-x}$S (12.0nm)</td>
</tr>
<tr>
<td>425°C, 0 min.</td>
<td>Fe$_2$C (25%)</td>
<td></td>
</tr>
<tr>
<td>Fe(CO)$_5$ precursor</td>
<td>Iron oxide/FeOOH (49%)</td>
<td></td>
</tr>
<tr>
<td>Coprocessing Residue Fe$_{1-x}$S (95%)</td>
<td>Fe$_{1-x}$S (95%)</td>
<td>Fe$_{1-x}$S (20.5nm)</td>
</tr>
<tr>
<td>425°C, 60 min.</td>
<td>Iron oxide (5%)</td>
<td></td>
</tr>
<tr>
<td>Fe(CO)$_5$ precursor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coprocessing Residue Fe$_{1-x}$S (~100%)</td>
<td>Fe$_{1-x}$S (~100%)</td>
<td>Fe$_{1-x}$S - trace</td>
</tr>
<tr>
<td>425°C, 1 hr.</td>
<td>Iron oxide (trace)</td>
<td></td>
</tr>
<tr>
<td>No catalyst added</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illinois #6 coal - Before Reaction</td>
<td>Pyrite (87%)</td>
<td>FeS$_2$ - trace</td>
</tr>
<tr>
<td></td>
<td>FeSO$_4$·H$_2$O (8%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ferric sulfate (5%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FeOOH (trace)</td>
<td></td>
</tr>
</tbody>
</table>

(solvent), and Fe(CO)$_5$ in an autoclave to decompose the precursor into small particles, some of which would end up on the carbon support. The TEM/STEM images of this catalyst system revealed a wide distribution of particle sizes, with many particles between 10-100nm. Energy dispersive analysis of the X-rays emitted from the sample confirmed that the small particles which were observed contained iron, while the matrix as well as the activated carbon blank contained no detectable iron. A typical micrograph is shown in Figure 2, exhibiting the iron-bearing particles (small, dark spots) on the more transparent background of the larger activated carbon particle.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of Frank Huggins for performing the Mössbauer spectroscopy, Cole van Ormer and J.R. Blachere for the electron microscopy, and funding support from the U.S. Department of Energy under grant number DE-FC22-88PC8806.
REFERENCES

Figure 1. Coal Conversion vs. Amount of Fe(CO)$_2$ Precursor

Figure 2. TEM/STEM Micrograph of Iron-Containing Particles Deposited on Activated Carbon by Thermal Decomposition of Fe(CO)$_5$
THE EFFECT OF MILD ALKYLATION PRETREATMENT ON LIQUEFACTION REACTIVITY OF ARGONNE COALS

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Colorado School of Mines
Golden, Colorado 80401

INTRODUCTION

Much of the recent research in direct coal liquefaction seeks to develop methods for dissolving coal at low reaction severity (perhaps defined as temperatures below 350 °C and pressures of 1000-1500 psig). Researchers at the Pittsburgh Energy Technology Center (1), the North Dakota Energy Research Center (2), Carbon Resources, Inc. (3), and the Colorado School of Mines (4) have investigated various methods for improving coal reactivity and liquid yields at mild reaction conditions. These studies showed that coal can be readily converted to THF soluble products via selective chemical attack rather than thermal bond scission, but that the rate and extent of coal dissolution at mild conditions is strongly dependent upon intrinsic coal reactivity. Thus the problem of optimizing low severity liquefaction performance becomes one of maximizing coal reactivity at these conditions.

The objective of this paper is to describe our efforts to improve intrinsic coal reactivity using mild acid-catalyzed alkylation as a pretreatment prior to liquefaction. The basis for this work derives from studies by Sternberg (5), Larsen (6), Sharma (7), and others where alkylation was utilized as a method for rendering coal soluble in THF or toluene to aid in structural analysis. Results from Sharma's work are particularly pertinent, since they demonstrate the ability to alkylate coal using alkyl alcohols rather than exotic and expensive chemical reagents such as tetrabutylammonium hydroxide, aluminum trichloride, methyl iodide, etc. Limited work has been reported which relates increased solvent solubility of alkylated coal to enhanced liquefaction reactivity. Schlosberg et al. (8) measured the reactivity of mildly alkylated Wyodak subbituminous and Illinois #6 bituminous coals in tetralin at 427 °C, 1500 psig hydrogen pressure and 130 minutes reaction time. A 10-21 wt% (MAF and alkyl group-free basis) increase in cyclohexane soluble conversion was noted for the alkylated coals.

EXPERIMENTAL PROCEDURE

Pocahontas low volatile bituminous coal, Illinois 6 high volatile bituminous coal, Wyodak subbituminous coal, and Beulah-Zap lignite from the Argonne Premium Sample Bank were used as feed coals in these experiments. Ultimate analyses for these coals are listed in Table I. Table II summarizes the alkylation reaction conditions studied. Each experiment was performed at ambient conditions by suspending 5 g of coal in 40 cm³ of alkyl alcohol and 0.1 cm³ of concentrated H₂SO₄ catalyst. After the prescribed reaction time, remaining alcohol was removed by roto-evaporation followed by vacuum drying (50 °C, 24 hrs.). Untreated coal samples were vacuum dried at the same conditions before liquefaction. Carbon analyses were performed on each alkylated coal sample using a Carlo-Erba model 1106 CHN analyzer.
to measure the extent of alkylation as computed from the following formula:

\[
\text{Extent of alkylation} = \frac{C_3 - C_1}{C_2 - C_3} \times 100
\]

where: 
- \(C_1\) = wt% carbon (MAF basis) in untreated coal
- \(C_2\) = wt% carbon in alkyl group
- \(C_3\) = wt% carbon (MAF basis) in alkylated coal

Liquefaction reactivity experiments were conducted in a 20 cm³ tubing bomb reactor attached to an agitator and immersed in a fluidized sandbath. Table III lists reaction conditions used in these runs. A non-hydrogen donor vehicle (1-methylnaphthalene) and a hydrogen donor vehicle (9,10-dihydrophenanthrane) were used as solvents (2/1 solvent/coal ratio). Coal conversion was monitored using tetrahydrofuran (THF) extraction data corrected for the intrinsic THF solubility of untreated and alkylated coals.

Solubility measurements were conducted at ambient conditions and consisted of: 1) sonicating the liquid products from the tubing bomb reactor in excess THF, 2) centrifuging the mixture, and 3) decanting THF-soluble products and excess THF from the THF-insoluble residuum. This procedure was repeated at least two times or until no additional THF-insoluble products were recovered. The THF insolubles were vacuum-dried (100 °C, 24 hrs) to remove residual THF, weighed, and finally ashed. Coal conversion to THF soluble products was computed as follows:

\[
\text{Coal conversion} = \frac{M_f - M_p}{M_f} \times 100
\]

where: 
- \(M_f\) = mass of MAF THF-insoluble coal charged
- \(M_p\) = mass of MAF THF-insoluble products recovered (corrected to satisfy the ash balance)

Photoacoustic Fourier Transform Infrared Spectroscopy (PAFTIR) was used to monitor functional group changes within the coal resulting from alkylation. The photoacoustic technique allows direct measurement of powdered solid state spectra without errors caused by low transmittance signals or variations in surface morphology. PAFTIR spectra generally measure solid properties to depths of about 40 angstroms.

RESULTS AND DISCUSSION

ALKYLATION STUDIES

Experiments were completed to study the effects of coal rank, alkyl group size, reaction time, and acid catalyst concentration on the extent of coal alkylation. Results from several of these runs are shown in Table IV. As mentioned earlier, all pretreatment studies were conducted at ambient temperature and pressure. The extent of alkylation increased with decreasing coal rank and roughly in proportion to each coal's oxygen content. As discussed later, this observation can be attributed to O-alkylation at phenolic and carboxylic sites in the coal. The extent of alkylation for Wyodak coal was less than 1.0 alkyl groups/100 carbon atoms using methanol or ethanol, but increased dramatically with n-propanol, n-butanol, or isobutanol. Other experiments using higher alcohols suggested that no
significant improvement in the extent of alkylation would be achieved over that obtained with n-propanol.

Approximately 50% of the ultimate extent of Wyodak coal alkylation was achieved in 30 minutes time, suggesting that highly reactive phenolic and carboxylic sites in the coal can be alkylated very quickly. The extent of alkylation increased with increased acid concentration below about 1.0 vol%. Higher acid concentrations had little effect on the extent of alkylation. Thus, it appears possible to mildly alkylate coal by varying the alkyl alcohol, reaction time, and acid concentration used.

Liquefaction Reactivity Studies
To study the effect of mild alkylation on liquefaction reactivity, samples of the four Argonne coals propylated for 3 hours with 1.0 vol% sulfuric acid catalyst were liquified in 1-methylnaphthalene solvent at low severity reaction conditions. Conversion results for these runs are summarized in Figure 1. Data for the corresponding untreated Argonne coals are included in this figure for ease of comparison. Propylation of each coal enhanced conversion to THF soluble products, although the effect increased dramatically with decreasing coal rank. A rough correlation was noted between the extent of propylation and improvement in liquefaction reactivity.

Figure 2 shows results from a series of low severity experiments using Wyodak coal which was alkylated with methanol, ethanol, n-propanol, n-butanol, and isobutanol (3 hrs, 1.0 vol% acid). These data suggest only a slight effect of alkyl group chain length on reactivity enhancement indicating that cheaper, commodity alcohols such as methanol may be used successfully as alkylating agent. This result indicates the potential for considering mild alkylation pretreatment on a larger process scale, although net methanol consumption must be better estimated before costs associated with alkylation pretreatment can be determined.

Finally, Figure 3 shows the effect of reaction temperature on the liquefaction reactivity of methylated (3 hrs, 1.0 vol% acid) and untreated Wyodak coals using DHP solvent. Clearly, mild alkylation pretreatment enhances reactivity over a range of conversion levels. This result is significant since it shows that mild alkylation may be a beneficial pretreatment even at conversion levels of commercial interest.

PAFTIR Studies
In an attempt to begin studying the reaction mechanisms governing our mild alkylation process, we analyzed each untreated and alkylated coal using Photoacoustic Fourier Transform Infrared Spectroscopy. Figure 4 shows the subtractive spectrum (alkylated coal spectrum minus untreated coal spectrum) for propylated Wyodak coal (3 hrs, 1.0 vol% acid). Several important features of this spectrum can be identified: 1) reduced O-H stretching in the 3200-3600 cm⁻¹ region, 2) increased aliphatic C-H stretching between 2800 and 3000 cm⁻¹, 3) appearance of the C=O ester stretch near 1700 cm⁻¹, 4) disappearance of the C=O carboxylate stretch near 1550 cm⁻¹, and 5) appearance of C-O aliphatic and aromatic stretches near 1000 cm⁻¹.

These observations are consistent with the dehydration and esterification reactions shown in Figure 5. Both reactions act to reduce hydrogen bonding within the coal structure which may have a direct positive impact on liquefaction reactivity. More indirectly,
these reactions lower the concentration of OH species in coal-derived products and hence, reduce the extent of retrogressive condensation via ether bridge formation. Reducing production of THF-insoluble condensation products increases the net THF-soluble coal conversion measured during the liquefaction experiment. What is unknown at this point is why such a small extent of reaction (perhaps less than 20\% of the OH groups are typically alkylated) results in significant reactivity enhancement. None of the spectra collected have shown any significant evidence of C-alkylation.

SUMMARY AND CONCLUSIONS

Acid-catalyzed alkylation pretreatment of four Argonne coals using alkyl alcohols has been investigated as a method for improving liquefaction reactivity. The extent of alkylation increased with decreasing coal rank and, to some extent, increasing alkyl group size. Infrared spectroscopic studies of the treated and untreated coals indicated that alkylation occurred at phenolic and carboxylic sites within the coal, but no evidence of C-alkylation was noted. Mild alkylation pretreatment improved liquefaction reactivity for each coal studied over a range of reaction severity. The improvement in liquefaction reactivity correlated roughly with the extent of alkylation achieved.

ACKNOWLEDGEMENT

The authors wish to acknowledge financial support from the U.S. Department of Energy under Contract No. DE-AC22-88PC88812.

REFERENCES CITED

Table I
ULTIMATE ANALYSIS OF FEED COALS

<table>
<thead>
<tr>
<th>Wt% Dry Basis</th>
<th>Illinois #6</th>
<th>Pocahontas #3</th>
<th>Wyodak</th>
<th>Beulah-Zap</th>
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</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>65.7</td>
<td>86.7</td>
<td>68.4</td>
<td>65.9</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.2</td>
<td>4.2</td>
<td>4.9</td>
<td>4.4</td>
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<tr>
<td>Nitrogen</td>
<td>1.2</td>
<td>1.3</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4.8</td>
<td>0.7</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8.6</td>
<td>2.3</td>
<td>16.3</td>
<td>18.2</td>
</tr>
<tr>
<td>Ash</td>
<td>15.5</td>
<td>4.8</td>
<td>8.8</td>
<td>9.7</td>
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<tr>
<td>Coal Rank</td>
<td>HVB</td>
<td>LVB</td>
<td>Subbit.</td>
<td>Lignite</td>
</tr>
</tbody>
</table>

Table II
ALKYLATION REACTION CONDITIONS STUDIED

Temperature: ambient (approx. 25 °C)
Pressure: ambient (approx. 0.85 atm)
Reaction Time: 0.5 - 24 hours
Alkylating Agent: methanol, ethanol, n-propanol, n-butanol, isobutanol
Catalyst: sulfuric acid (0.1 - 3.0 vol%)
Table IV
RESULTS OF AMBIENT ALKYLATION PRETREATMENT EXPERIMENTS

<table>
<thead>
<tr>
<th>Coal*</th>
<th>Alcohol</th>
<th>Time (hrs.)</th>
<th>Conc. (vol%)</th>
<th>Acid Extent of Alkylation (groups/100 C atoms)</th>
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</thead>
<tbody>
<tr>
<td>Ill.</td>
<td>n-propanol</td>
<td>3.0</td>
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<tr>
<td>Poc.</td>
<td>n-propanol</td>
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<td>1.0</td>
<td>3.8</td>
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<td>B-Z.</td>
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<td>Wyo.</td>
<td>ethanol</td>
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<td>1.0</td>
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<tr>
<td>Wyo.</td>
<td>n-butanol</td>
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</tr>
<tr>
<td>Wyo.</td>
<td>isobutanol</td>
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<td>3.0</td>
<td>2.0</td>
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</tr>
<tr>
<td>Wyo.</td>
<td>n-propanol</td>
<td>3.0</td>
<td>3.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

* Ill. = Illinois #6  
  Wyo. = Wyodak  
  Poc. = Pocahontas #3  
  B-Z = Beulah-Zap

Figure 1. Effect of Propylation on Argonne Coal Liquefaction Reactivity at Low Severity Conditions
Figure 2. Effect of Alkyl Group Addition on Low Severity Wyodak Coal Liquefaction Reactivity

Figure 3. Effect of Reaction Temperature on Liquefaction Reactivity of Methylated and Untreated Wyodak Coal
Figure 4. Subtractive Spectrum of Propylated Wyodak Coal Collected Using Photoacoustic Fourier Transform Infrared Spectroscopy

Figure 5. Phenolic Dehydration and Carboxylic Acid Esterification Reactions Occurring During Mild Alkylation Pretreatment
USE OF DISPERSED CATALYSTS FOR COAL LIQUEFACTION


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ABSTRACT
We have briefly explored the use of dispersed catalysts for conversion of an Illinois #6 into soluble products. We compared both supported and non-supported catalysts and found that the non-supported catalysts gives superior conversions. The non-supported catalysts were impregnated into the coal by use of either aqueous metal salts or organic solutions of organometallic complexes. The organometallic precursors were found to be exceptionally active and provide the greatest yields of toluene soluble products. Our key to effective dispersed catalysts is the use of a soluble sulfido complex that does not require high temperature activation.

INTRODUCTION
Although great progress has been made in converting coal to distillable liquids in high yields, the products are still not competitive with petroleum. A major problem is that under the severe conditions for bond-breaking during coal liquefaction, regressive reactions take place that produce char and coal liquids that are difficult to hydrotreat (1-6). For instance, phenolics are thought to polymerize into polymeric furans during the liquefaction process. In a similar manner, these coal liquids are high in nitrogen heterocycles. These heterocyclic oxygen and nitrogen containing molecules make coal liquids difficult to upgrade. In order to hydrotreat these materials such high temperatures and hydrogen pressures are required, that the valuable aromatic containing materials in the coal liquid are concurrently hydrogenated. In past work, we have concentrated on developing highly dispersed highly active catalysts to hydrotreat these coal liquids with the minimum consumption of hydrogen (7-11). In this work we look at the feasibility of using similar techniques to impregnate the coal with highly dispersed catalysts for improved liquefaction that give less regressive reactions.

Dispersed catalytic liquefaction has several distinct advantages over conventional thermal or catalytic liquefaction. In the presence of hydrogen, a suitably dispersed catalyst can provide a highly reducing environment within the coal matrix, thus eliminating the need for a good hydrogen donating solvent. An added advantage to these catalysts is that they can promote certain bond cleavage reactions during the liquefaction step. If they can aid in removing the heteroatoms, namely oxygen and nitrogen, during the early stages in coal liquefaction, then the detrimental regressive reactions would be minimized. Thus a better quality coal liquid product would be produced that would be easier and less expensive to hydrotreat.

Many workers have investigated non-supported high dispersion catalysts (12-21). Most work on dispersed catalysts has focused on metal salts such as ammonium molybdate or iron.

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sulfides, or oil soluble catalysts such as molybdenum naphthalate. Derbyshire et al. have conducted considerable research utilizing the (NH₄)₂MoO₄ and (NH₄)₂MoS₄ aqueous impregnation methods at low temperatures where they have shown that these dispersed catalysts can effectively utilize hydrogen to aid in subsequent conversions (13-15). The problem with most dispersed catalysts that have been tested is that they are only activated at high temperatures. For instance, molybdenum tetra(thiolate) decomposes to MoS₃ at low temperatures. However, the more active form is MoS₂ which is formed at much higher temperatures (≥350°C) (22,23). In a similar manner, the molybdenum naphthalate needs to be transformed into MoS₂. The importance of the correct stoichiometry has been emphasized by Montano et al. (24,25). They have suggested in work on iron sulfide catalysts that the pyrite (Fe₅S₉) must be transformed to pyrrhotite, Fe₃S₅ (0<x<0.125) before it is catalytically active. Under coal liquefaction conditions, the sulfur must diffuse out of the pyrite to allow the transformation to occur. In contrast, when the precursor is Fe(CO)₅, sulfur diffuses into the iron to form highly dispersed pyrrhotite.

Since we have been successful in increasing the activities of hydrotreating catalysts by use of organometallic precursors to form highly dispersed catalysts, we are very interested in using these same techniques for direct liquefaction catalysis (7-11). Our goals are to synthesize and test soluble complexes that are as close to the correct stoichiometry and structure of the active catalyst during the coal liquefaction. Thus we hope that our catalysts, since they do not require high temperature activation, will cause bond breaking reactions at lower temperatures than are currently possible with dispersed catalysts, and may therefore aid in reducing regressive reactions.

**EXPERIMENTAL**

The procedure for converting coal in terialin is as follows. For the experiments involving aqueous pretreatment, the coal was pre-treated by placing approximately 5 g of coal, 0.003 moles catalyst and 10 mL of distilled water in a 45-mL Parr bomb with a Teflon insert. The reactor was purged and pressurized with 500 psi of nitrogen and inserted into a preheated furnace for 30 min at 250°C. After the reactor had cooled, the insert was removed, and transferred into a centrifuge tube fitted with a screw cap. The aqueous layer was removed after centrifuging the mixture, and the pretreated coal washed twice with distilled water. The wet coal was mixed with 30 g of tetralin and then transferred to a 300 mL Autoclave Engineers Magnedrive autoclave. Nitrogen, although brief exposure of the premeated mal to air during the transfer could not be avoided. The autoclave was then purged and pressurized with 500 psi of hydrogen and heated at 400°C. The electric furnace could be raised or lowered by use of a remotely controlled jack. The typical heat-up time was 30 min. After 20 min reaction the heater was immediately lowered. The removal of the furnace gave a rapid cool down of about 100°C in about 5 minutes. After the reaction had cooled, the coal liquid and residue were taken up in tetrahydrofuran (THF). The THF was removed under reduced pressure and the residue taken up in toluene. The product was filtered through a medium porosity filter and separated into toluene soluble (TS) and insoluble (TI) fractions. The toluene and residual tetralin were then removed from the TS under reduced pressure. The TS and TI fractions were then dried at 76°C for 12 h under vacuum (<0.1 mm).

**RESULTS AND DISCUSSION**

This work was conducted in order to demonstrate that there is a correlation between our hydrogenolysis results and our liquefaction results due to the means of catalyst preparation. We feel the development of hydrotreating catalysts as important, since a good hydrogenolysis catalyst, should also be a good coal liquefaction catalyst. We have prepared these highly dispersed catalysts by impregnating homogeneous organometallic complexes on the support. The advantage of these
methods are that one can create "surface confined" highly dispersed, small particle sized catalysts throughout the support. In contrast, the conventional incipient wetness technique tends to cause large metal clusters to be formed, leaving a low surface area of active catalyst, and thus much less activities.

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The coal liquefaction experiments were conducted with a high ratio of tetratin to coal (6 to 1). Therefore, we would expect that the effect of the catalyst in terms of providing a reducing environment or forming an active solvent should be minimized. Thus, any differences we see in conversions should primarily reflect the effect of the catalyst promoting bond breaking reactions. (although one could argue that the catalyst is producing low concentrations of reactants derived from the solvent that are actually producing the bond breaking).

Table 2 lists some of our results for conversion of coal into toluene soluble material. The conversion is calculated from the insoluble material corrected for the ash content. Molybdenum tetrahalide was chosen since it is an excellent hydrogenation and liquefaction catalyst precursor and also can be used to form mixed metal sulfide clusters which may be used as hydrogenolysis catalysts. One question to be addressed for the water soluble molybdenum salt was the optimum method of preparation. We thought that the ideal way to impregnate the coal is the mix the coal in an aqueous solution of the thiomolybdate salt, and heat the solution at 250°C for 30 min. This hot aqueous impregnation is thought to swell the coal, and thus allow better impregnation with the aqueous catalyst. Experiments 1-3 in Table 2 show the results after this aqueous impregnation. In the first experiment, the coal was impregnated and then dried under vacuum at 76°C to remove the water. In the second experiment, the coal was impregnated, centrifuged to remove the excess water, and the immediately placed in the autoclave. In the third experiment, the molybdate salt was dissolved in 4 mL of water, and added to the coal with tetratin, without any impregnation. As shown in this table, experiment 1 gave a low conversion (41%), compared to experiments 2 and 3 (51%). When the coal was dried, the molybdenum catalyst may have become larger in cluster size or allowed crosslinking in the coal matrix to occur.

For comparison, we chose two organometallic molybdenum dimers. A sulfido complex, CppMo2(μ-SH)2(μ-S)2, and a molybdenum acetate dimer, Mo2(OAc)4. As shown in experiments 4 and 5, respectively, the sulfido dimer provides a much higher conversion than the aqueous impregnation methods, (61% compared to = 50%), and also a higher conversion than the non-sulfided Mo2(OAc)4 catalyst (55%).
CONCLUSIONS

We view this enhancement with the organometalic complexes as the ability to be better dispersed than the aqueous impregnation techniques, in a similar manner as demonstrated in our hydroreacting results. The highest activity with the sulfido complex, we believe, is because the catalyst was impregnated in a highly active form, and thus does not require subsequent activation during the liquefaction step. Thus the advantages of our methods are (1) the catalyst can be readily impregnated into the coal and (2) we can design a catalyst such that it transforms directly into the correct stoichiometry for the active form of the catalyst. In future work we hope to investigate the scope of these highly active catalysts, and prepare soluble mixed metal clusters which should enhance the liquefaction of coal still further.

ACKNOWLEDGEMENTS

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REFERENCES

Table 1

TURNOVER FREQUENCIES FOR QUINOLINE HDN

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<thead>
<tr>
<th>Catalyst</th>
<th>Precursor</th>
<th>THO</th>
<th>PCH</th>
<th>PB</th>
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<tr>
<td>NiMo</td>
<td>Conv</td>
<td>67.4</td>
<td>8.2</td>
<td>0.3</td>
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<tr>
<td>NiMo(OM)</td>
<td>Mo_2(OAc)_4</td>
<td>41</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>NiMo(OM)</td>
<td>Mo_2(allyl)_4</td>
<td>111</td>
<td>26.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

aReaction of 10 mL of 0.0197 M quinoline in n-hexadecane and 0.100 g catalyst at 350°C and 500 psig H₂.

bTF - moles reactant or product/total moles metal/h

Table 2

CATALYZED TETRALIN CONVERSIONS

<table>
<thead>
<tr>
<th>No</th>
<th>Pretreatment</th>
<th>% TS</th>
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<tr>
<td>1</td>
<td>MoS_2/Dried</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>MoS_2/4 mL</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>MoS_2/Wet</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>Cp_2Mo_2(μ-SH)_2(μ-S)_2</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>Mo_2(OAc)_4</td>
<td>56</td>
</tr>
</tbody>
</table>

aReaction conducted in 300-mL autoclave of 5 g coal in 30 g of tetralin and 500 psi H₂ at 400°C/20 min.
bSolubility based on wt % insoluble material, corrected for ash.
cCoal was dried at 76°C under vacuum after aqueous molybdenum impregnation.
dMolybdenum was dissolved in water (4 mL) added to the coal/tetralin mixture.
eCoal was impregnated with aqueous molybdenum, and transferred to the autoclave while wet.
INTRODUCTION

Fundamental studies of the mechanism of catalytic coal conversion not only provide an understanding of how current catalysts work but also offer the prospect of designing better catalysts in the future. One approach to the study of catalysis is to observe the production of products from single, known probe compounds. This approach is especially useful when the products can be shown to arise only from particular reactive intermediates, such as cations or radicals.

Three probes were used to investigate the mechanism of catalysis of a dispersed molybdenum sulfide catalyst. The 1,5-dimethylnaphthalene (1,5-DMN) was selected because of its ability to distinguish three important types of reactions (Figure 1). Under cationic conditions, the methyl groups of 1,5-DMN migrate to form 1,6-DMN and subsequently 2,6-DMN. Each isomer will react to give an equilibrium mixture of all three isomers, but the 1,5-DMN is the least stable and thus is the most sensitive probe for a cationic environment. The 1,5-DMN can also undergo demethylation to form 1-methylnaphthalene (1-MN). This reaction can be envisioned as occurring either via a cationic cracking mechanism or via an ipso substitution by a hydrogen atom; however, the evidence given below supports a radical ipso substitution under our conditions. The third reaction of 1,5-DMN is hydrogenation. This leads to the formation of 1,5-dimethyltetralin (1,5-DMT). Thus, three reaction types of interest in catalytic coal conversion are distinguished by this probe. In addition, decalin and tricyclodecane (Figure 2) were used to distinguish hydrogen abstraction reactions. The results obtained from these three probes provide a description of the reaction environment present during catalytic coprocessing.

Other workers at the PETC have shown molybdenum trisulfide prepared by the method of Eggertsen and Roberts to be an effective coprocessing catalyst. Reactions of the probe compounds in the presence of this catalyst were compared to the reactions observed in the presence of a known cationic catalyst and a known radical initiator. These reference additives were selected to ensure that the probes would indeed distinguish the different reaction environments. Bibenzyl generates free radicals by a thermolytic dissociation to form stoichiometric amounts of benzyl.
These radicals abstract hydrogen from solvent and solute, and thus provide a pool of radicals of varying activity. Benzyl radicals also abstract hydrogen atoms from gas phase hydrogen, producing hydrogen-atom-mediated hydrocracking. A commercial cracking catalyst (D980-13) was selected because of the known acidic character of silica-alumina catalysts. Thus, a comparison of the reactions of the probes in the presence of the molybdenum sulfide with the reactions in the presence of the reference additives provides information about the reaction environment generated by the coprocessing catalyst.

EXPERIMENTAL

The commercial silica alumina (D980-13) was obtained from W.R. Grace (grade 980-13, 13% alumina) as an extrudate. The friable solid was ground with a mortar and pestle, and oven-dried at 150°C overnight. The molybdenum trisulfide was prepared from ammonium tetrathiomolybdate by precipitation from an aqueous solution using formic acid. This procedure is best carried out in a hood because of the hydrogen sulfide formed.

All reactions were performed using 40-mL 316-stainless steel reactors. The 8-gram reaction mixtures contained the probe (200 mg); a silica-alumina (10 mg), molybdenum trisulfide (10 mg), or bibenzyl (2.0 g) additive; and n-octacosane solvent. The reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and shaken at temperature for 60 minutes. The products were washed from the cooled reactor using inhibitor-free tetrahydrofuran (Aldrich 27,038-5) and were analyzed by GC-MS.

RESULTS

The reactions of 1,5-DMN are shown in Figure 1. The amounts of the products obtained in the presence and absence of the three additives are given in Table I. The effect of the added bibenzyl is to increase the yield of 1-MN because of the increased production of hydrogen atoms. Significantly, no isomerization of the methyl groups is seen in the blank or in the presence of the free radical initiator, nor is the hydrogenation to 1,5-DMT an important reaction under these conditions. In the presence of the acidic catalyst, D980-13, the isomerization of the methyl groups becomes the predominant reaction. Of the recovered dimethylnaphthalenes, 83% have at least one methyl group in a beta position. The 1,5-DMN is indeed sensitive to the presence of the acidic sites of this catalyst. Both 1-MN and 2-MN are obtained as the demethylated products. The total amount of demethylation is the same as was seen in the absence of catalyst, about 10%. In this case, it is reasonable to assume that the cationic mechanism is superimposed on the background radical reaction. The
1,5-DMN can rearrange via a cationic mechanism, and the isomers thus produced can subsequently crack by a hydrogen atom mechanism. In addition, the 1-MN and 2-MN formed from the cracking can be interconverted by the acid catalyst. Again, no effect is seen on the amount of hydrogenation, which remains low. The results obtained in the presence of the molybdenum trisulfide catalyst are shown in the last column of Table I. Molybdenum disulfide is assumed to be the actual form of the catalyst under liquefaction-like conditions. The effect of adding this catalyst is to increase the extent of hydrogenation to form the dimethyltetralin. The molybdenum catalyst does not exhibit cationic behavior, as evidenced by the lack of isomerization of the methyl groups, nor does it increase the extent of hydrocracking to form methylnaphthalene. The lack of cationic activity was initially surprising because single crystal experiments at lower temperatures have associated carbonium ion intermediates with the basal plane of molybdenum disulfide. However, a similar lack of isomerization has been noted during the cracking of 1-methylnaphthalene in the presence of a supported CoMo catalyst at slightly higher temperatures.

In addition to the aromatic hydrocarbon probe, two alicyclic hydrocarbons, decalin and tricyclo[5.2.1.0\(^2\)\(^6\)]decane (TCD), were used as probes (Figure 2). The isomerization of cis- to trans-decalin requires the removal of a tertiary hydrogen, whereas the isomerization of endo- to exo-TCD requires the removal of a secondary hydrogen. The effects of the isomers (more stable / less stable) after reaction in the presence and absence of the three additives are given in Table II. The effect of added bibenzyl is to increase the extent of isomerization of both probes. The radical isomerization of the decalin is known to occur under these conditions, but the radical isomerization of the TCD was surprising. In general, Wagner-Meerwein rearrangements are not observed for radicals. One exception is the recently reported radical isomerization of homoadamantane to methyladamantane. The addition of the D980-13 acidic catalyst had no effect on the isomerization of the TCD, but it did cause an increase in the extent of the isomerization of the decalin. Apparently the decalin can isomerize by either hydrogen atom or hydride abstraction. The results obtained from the molybdenum sulfide are very similar to the results from the D980-13 catalyst for this set of probes. The isomerization of the TCD is unaffected, but the isomerization of the decalin is accelerated.

DISCUSSION

The results obtained from the three probes are summarized in Table III. The catalysts are considered to either promote (+) or not promote (-) the reactions listed. Aromatic methyl group hydrocracking is promoted only by bibenzyl and is thus proceeding via an ipso substitution by a hydrogen atom. The lack of crack-
ing in the presence of the D980-13 catalyst is likely due to the difficult formation of methyl cations. The isomerization of endo-TCD is also catalyzed only by the bibenzyl and is therefore proceeding via a radical hydrogen abstraction from a secondary carbon. If free radicals are formed in the presence of the molybdenum sulfide, they are not energetic enough to react with gas phase hydrogen to form the hydrogen atoms, nor are they energetic enough to abstract the secondary hydrogen from the TCD. This means they have to be considerably less reactive than the benzyl radicals formed from the bibenzyl.

Since the isomerization of the 1,5-DMN is catalyzed only by the D980-13 acidic catalyst, it is probably proceeding via a cationic mechanism similar to that found in the presence of solution phase acids. The absence of this isomerization for the molybdenum sulfide indicates either that there are few acid sites of sufficient strength to catalyze the isomerization, or that the active sites are not accessible to the 1,5-DMN. Other sites of lower acidity may be present.

All three additives are capable of increasing the amount of isomerization of decalin. At least two mechanisms are operative. In the presence of a radical initiator, the isomerization is driven by the abstraction of a hydrogen atom from the tertiary carbon. In the presence of the acid catalyst, a similar mechanism involving hydride abstraction would account for the increased isomerization. Isomerization occurs also in the presence of the molybdenum sulfide. Since the molybdenum catalyst shows no activity in the other radical and cationic reactions above, it may be catalysing the isomerization by yet a third mechanism. Dehydrogenation of the cis-decalin by loss of one tertiary hydrogen and an adjacent secondary hydrogen leads to an octalin with the double bond to the bridgehead carbon. Subsequent hydrogenation from the opposite side leads to the trans-decalin. The feasibility of a dehydrogenation - hydrogenation mechanism is strengthened by the observed hydrogenation activity described next.

Only the molybdenum sulfide was effective in hydrogenating the naphthalene ring to form tetralin. The absence of concomitant radical or cationic reactions indicates that the hydrogenation is probably proceeding via a surface-bound intermediate or a concerted addition of hydrogen. Based on the information provided by these probes, the effectiveness of the molybdenum sulfide catalyst in coprocessing may lie in the fact that it provides hydrogenation activity but does not introduce strong acid sites associated with coke formation nor does it promote radical formation, which has been associated with retrogressive reactions. The possible presence of weaker acid sites, capable of cracking other alkyl chains, is being investigated.
CONCLUSIONS

Probe compounds have been used to explore the mechanism of catalysis of a molybdenum sulfide known to be active for the coprocessing of coal and oil residua. Under typical coprocessing conditions, the sulfide displayed predominately hydrogenation activity. Comparison with additives known to be sources of radical and cationic activity provided no evidence that the molybdenum catalyst has either of these properties.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

ACKNOWLEDGMENT

The authors thank Malvina Farcasiu for bringing reference 10 to their attention.

REFERENCES

### TABLE I. Normalized Distribution of Products from 1,5-Dimethyl-naphthalene.

<table>
<thead>
<tr>
<th>ADDITIVE</th>
<th>None</th>
<th>Bibenzyl</th>
<th>D980-13</th>
<th>MoS₂³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5-DMN</td>
<td>83%</td>
<td>48%</td>
<td>15%</td>
<td>66%</td>
</tr>
<tr>
<td>1,6-DMN</td>
<td>1%</td>
<td>1%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>2,6-DMN</td>
<td>0</td>
<td>1%</td>
<td>33%</td>
<td>0</td>
</tr>
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<td>1-MN</td>
<td>13%</td>
<td>38%</td>
<td>6%</td>
<td>14%</td>
</tr>
<tr>
<td>2-MN</td>
<td>0</td>
<td>1%</td>
<td>8%</td>
<td>0</td>
</tr>
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<td>NAP</td>
<td>0</td>
<td>8%</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>DMT</td>
<td>4%</td>
<td>2%</td>
<td>0</td>
<td>17%</td>
</tr>
</tbody>
</table>

Note: DMN = Dimethylnaphthalene  
MN = Methylmnaphtalene  
NAP = Naphthalene  
DMT = Dimethyltetralin

### TABLE II. Comparison of the Extent of Isomerization of cis-Decalin and endo-Tricyclo[5.2.1.⁰²]decane.

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>TCD</th>
<th>EXO / ENDO</th>
<th>DECALIN</th>
<th>TRANS / CIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.31</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bibenzyl</td>
<td>1.38</td>
<td>2.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D980-13</td>
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<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoS₂³</td>
<td>0.28</td>
<td>1.13</td>
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</tbody>
</table>

### TABLE III. Summary of Probe Reactions.

<table>
<thead>
<tr>
<th>Probe Reaction</th>
<th>Bibenzyl</th>
<th>D980-13</th>
<th>MoS₂³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-Group</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isomerization at 2° Carbon</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isomerization of Aromatic Alkyl-Group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isomerization at 3° Carbon</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>
FIGURE 1. REACTIONS OF 1,5-DIMETHYLNAPHTHALENE.
FIGURE 2. THE ISOMERIZATION OF DECALIN AND TRICYCLO[5.2.1.0^2.6]DECANE.
A MACROMOLECULAR NETWORK MODEL FOR COAL FLUIDITY
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Advanced Fuel Research, Inc. 87 Church Street, East Hartford, CT 06108

ABSTRACT
We have developed a model for coal fluidity based on the decomposition and condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions. The model is an extension of the FG-DVC model of coal pyrolysis. It employs a macromolecular network consisting of aromatic ring clusters linked by bridges. In the FG-DVC model, bond scissions are described by a single first order reaction with a distribution of activation energies, and crosslinking is related to CO₂ and CH₄ formation. The FG-DVC model predicts the yield of liquids produced during heating of the coal. The fluidity is dependent on the relative amounts of the liquid, (molecules detached from the network) and solid (the remaining network) and on the fluidity of the liquid component. The fluidity of the liquid component depends on the average molecular weight of the liquid and on the temperature. Excellent agreement has been obtained between the model predictions for fluidity and low temperature fluidity measurements of Oxley and Pitt, Fitzgerald and van Krevelen. Good agreement has been obtained at high temperatures between the model predictions and measurements of Fong for the onset of the fluidity and the peak fluidity value. The loss of fluidity, however, is predicted to occur sooner than is indicated by the data. The data covers over four orders of magnitude in fluidity and four coals with carbon concentration between 80 and 90%.

INTRODUCTION
When bituminous coals are heated, they can decompose sufficiently to become liquid. Those in the range of 82 to 89% carbon achieve the highest fluidity (1,2), but even lignites, if heated rapidly enough can exhibit some fluidity (3). The understanding and ability to predict a coal’s fluid properties is important in many processes. In liquefaction, highly fluid coals dissolve quickly in the process solvent so that further chemistry occurs by liquid/liquid interactions while non-fluid coals must undergo slower solid/liquid interactions. In combustion or gasification, fluidity controls particle swelling (4), agglomeration of particles, char reactivity (5), and subsequent fragmentation (6) of char. In coke making, fluidity controls the coke properties (7,8). Fluidity also affects the growth of carbon fibers from coal tars.

There are a number of factors which contribute to the fluidity of coal liquid. They include: i) the fluidity of the liquid part itself, with and without molecular entanglements; ii) the dependence of this fluidity on temperature; iii) the contributions of suspended solids in the liquid, both “chunks” of char, and mineral particles; and iv) the formation of a foam due to trapped gases.

Several models for coal liquid viscosity have been proposed which consider all of the influences except the trapped gases. The models were based on the two step process described by van Krevelen and coworkers (1,9), which assume the following reactions to occur on heating.

\[ k_1 \text{coal} \rightarrow k_2 \text{metaplast} \rightarrow \text{coke} \]

where \( k_1 \) and \( k_2 \) are reaction rate constants. In the viscosity models the change of fluidity is assumed to result only from the change in solids mass fraction, \( \phi_s \) (coal and coke) in the melt. Thus Bronowski et al. (10) used an expression in which fluidity was directly proportional to the mass fraction (1-\( \phi_s \)) of fluid (metaplast) present. Expanding on this, Fitzgerald (11,12) used an equation which described the relative fluidity as depending on fluid fraction raised to a power \( n \) (where \( n \) was chosen to be 2.5). This power law expression was based on earlier work by Roscoe (13) and Brinkman (14). In a similar manner, Fong et al. (15) used an expression put forward by Frankel and Acrivos (16), in which the fluidity also depends on a power of the fluid fraction. Their model has the

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extra feature of a critical solids-volume-fraction at which fluidity disappears. This critical value occurs at the maximum volume fraction that the solids can occupy as limited by particle-particle interaction. At this critical value, the liquid fraction is insufficient to separate the solid particles. Its value is 0.64 for randomly close-packed spheres, while it ranges from 0.5 to 0.9 for other systems, depending on particle shape and state of agglomeration (17). Viscosity models predict that the fluidity vanishes for volume fractions equal to or greater than the critical value, and we refer to this as the inhomogeneous gel point. The chosen critical value in Fong’s model was at a volume fraction of unity, somewhat higher than usual (17). A similar model was used by Oh (18). The above models gave good fits to data, although in each case the model parameters (k, k', n and the critical solids volume fraction) were chosen to fit data from a particular coal studied in a limited number of experiments covering a narrow range of heating rates, or holding temperatures.

Based on the observation that coal can be considered as a macromolecular network to which theories of crosslinked polymers may be applied (1,2,19,25,26), we have examined the polymer literature of viscosity in polymer melts (17,27-32). For non-reacting melts of branched polymers at molecular sizes below those sufficiently large for entanglements, there is experimental and theoretical support for viscosities which depend exponentially on side-arm molecular mass (27). These same authors determined temperature-dependent activation energies for viscosity, for temperatures below 200°C. It is noted that at higher temperatures (~ 600 K) Nazem found temperature independent activation energies for the viscosity of carbonaceous mesophase pitch (28).

In reacting melts, the manner in which average molecular weight varies with extent of reaction in a homogeneous melt has been considered in the branching theory described by Macosko and coworkers (29). Insofar as it describes molecular weight distributions, this theory duplicates and extends the results of older combinatorial methods developed by Flory (30) and by Stockmayer (31). A particular result of Macosko’s work is that measured viscosity correlates well with the weight average molecular weight of the largest linear path through the molecules. This theory predicts that the homogeneous gel-point (the point at which the viscosity goes to infinity) appears at the first occurrence of a solid phase.

It is not clear whether Macosko’s approach is appropriate for coal and it has not been tested. Coal is typically an inhomogeneous reacting melt where the reaction coal --> metaplast is the inverse of the polymerization, and metaplast --> coke is an example of repolymerization and crosslinking. The inhomogeneities result from several factors including: starting with a powdered solid (which would be sufficient to insure inhomogeneity), having a material consisting of diverse maceral types, and containing mineral grains. Theories which describe the viscosity of a suspension of a solid in a liquid, such as those mentioned above for coal, are general in their application (17,32), and also apply to suspensions of a solid in a polymer melt.

We have employed polymer concepts to describe tar and extract formation in coal pyrolysis, initially employing linear chain statistics (33,34) and subsequently employing network statistics (35-38). Our “DVC” model includes the processes of Depolymerization (bond breaking), Vaporization (mass transport), and Crosslinking. This model was combined with our functional group (FG) model for gas evolution (4,39-41) to provide the general FG-DVC coal pyrolysis model in which the crosslinking process is related to the evolution of certain gas species (42,43). The FG-DVC model employs Monte Carlo methods to compute the network properties. More recently, network models of thermal decomposition have been proposed employing percolation theory (44,45). We have also employed percolation methods for the statistical calculations in the FG-DVC model (46).

The fluidity model presented here employs the FG-DVC model to predict the molecular weight distribution of the decomposing macromolecular network. From this distribution, a solid fraction $\phi_s$ and a liquid fraction with a weight-average molecular weight are defined. These parameters are employed using the concepts of inhomogeneous mixtures to predict the fluidity from the solid fraction, the liquid viscosity and the temperature (17,28,32). The model predictions are compared with measurements made with a Gieseler plastometer (1,47,48) and with the high temperature fluidity measurements of Fong et al. (15).
EXPERIMENTAL

The low temperature fluidity data employed in this paper is literature data obtained with a Gieseler plastometer. Descriptions of the apparatus and operation may be found in the literature (49,50). The viscosity is determined by measuring the rotation rate of a stirrer in the sample when constant torque is applied. There are many problems of translating stirrer rotation speed to viscosity in poise and most researchers simply report data in degrees/min or dial divisions/min (DDPM) where one DDPM = 3.6°/min. Some data of van Krevelen was reported in poise (1). We have used these data in conjunction with data for the same coal reported in degrees/min to obtain the calibration

\[ 1°/\text{min} = 0.7 \times 10^6 \text{rhe's} \]

where 1 rhe = 1 poise.

In making fluidity measurements on coal, it has been found that there is an initial softening of coal on heating which is reversible, and has been associated with melting and hydrogen bond breaking. This is followed by a sharp rise in fluidity due to the decomposition of the macromolecular network due to covalent bond breaking, and it is from this point that our model seeks to describe the processes. This sharp rise is illustrated in Fig. 1 which presents the measured fluidity of a bituminous coal as a function of time as the coal was heated from 300°C at 3°C/min to 407°C and held at constant temperature (48). The slower fall in fluidity with time is due to crosslinking which resolidifies the network. This crosslinking rate is linearly correlated with the initial rate for the evolution of CH₄ (38,42,43,51).

The high temperature data was obtained by Fong et al. (15) in a device designed for rapid heating. Coal is contained in a pancake shaped cavity in which a disk driven at constant torque is allowed to rotate. The rotation speed was related to viscosity in poise using standards of known viscosity.

The model we present employs both the coal composition and the kinetic rates for bond breaking and gas evolution. The crosslinking rate is related to the gas evolution. Since it was not possible to obtain samples of the original coals used for the viscosity measurements we have selected from the Argonne coal sample collection, those which best match the reported coals in carbon concentration and volatile matter. Table I presents the available data on the coals whose viscosities have been measured and the Argonne coal used in the model. More complete composition data for the Argonne coals were presented by Voores (52). The previously determined kinetic rates and model parameters were presented by Serio et al. (41,53). A comparison of the weight loss at constant heating rate of the Argonne coals and the coals employed in the study of van Krevelen (1) is presented in Fig. 2.

THEORY

The theory of coal fluidity consists of two parts: i) a macromolecular network model (FG-DVC) to predict the liquid fraction and average molecular weight of the liquid as a function of time and temperature; and ii) empirical expressions to predict fluidity from the liquid fraction, the average molecular weight of the liquid and the temperature.

To predict the liquid fraction and its average molecular weight, we employ a model which describes the decomposition or condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions (42,43). Our model employs a sample macromolecular network in the computer consisting of aromatic ring clusters (monomers) linked by bridges. The bridges are either broken by bond scission reactions or are formed by crosslinking. As discussed previously (38,42,51), crosslinking occurs at low temperatures for low rank coals by a process apparently associated with CO₂ evolution. Crosslinking at moderate temperatures occurs by a process associated with CH₄ evolution. It is this process which leads to the reduction of fluidity shown in Fig. 1. The chemical justification for the association of crosslinking with CH₄ evolution is that the CH₄ is released by an ipso-substitution reaction involving a free radical connected to a ring cluster. Other peripheral groups may also be released in a similar manner.

A simple example of the model is shown in Fig. 3. Figure 3a shows the starting molecule. As explained previously (42,43), the number of branch points (initial crosslinks) is chosen to match the expected molecular weight between crosslinks. The length of the linear chains ε which are crosslinked is selected so that the fraction of unattached small monomer clusters matches the
measured fraction of pyridine solubles. The position of the bonds is randomly chosen. The molecular weight distribution is shown in Fig. 3b. When bonds are broken, more small molecules are formed as shown in Fig. 3c and 3d.

As discussed below, the viscosity is related to the liquid fraction produced during the break up of the network. The liquid fraction consists of all molecules detached from the starting macromolecular network (the solid fraction). Operationally we count the largest 3 molecules as belonging to the solid fraction and all others as belonging to the liquid fraction. This is a convenient approximation which gives results that agree reasonably well with experiment and do not depend on the molecular weight of the starting computer molecule. We have also used just the largest molecule as the solid fraction and found that computed results are similar but noisier.

An important feature of a homogeneous network model is that the break-up or solidification of the network occurs near a homogeneous "gel point" where the number of unbroken bonds per ring cluster (monomer), \( \alpha \), reaches a sufficiently low value. This gel point for a polymerizing melt occurs at the first appearance of the solid (or in the case of a decomposing network when the liquid fraction goes to 1.0) since the solid in a homogeneous melt extends throughout the entire melt. For most network geometries the break-up of the network occurs between \( \alpha = 1.0 \) and \( \alpha = 0.8 \).

For an inhomogeneous melt (such as expected for a liquefying powdered coal sample), the solids can appear as isolated particles so the gel point occurs at a higher solid fraction (lower liquid fraction). Based on the inhomogeneous model of fluidity discussed below, the liquid fraction must only exceed 0.3 before appreciable fluidity can occur. With the network geometry assumed for this model, this minimum liquid fraction is achieved at a critical value \( \alpha_c \) of 0.95. For bituminous coals, this critical value can be achieved in pyrolysis and the coal melts and becomes fluid. For low rank coals, the effects of low temperature crosslinking is to increase \( \alpha \) so that in some cases the network cannot come apart by normal pyrolytic reactions. Figure 4 compares the variation in \( \alpha \) with time at constant temperature for a lignite and a bituminous coal. Also shown are the individual contributions to the total bond count and resulting fraction of the network which becomes liquid. The value of \( \alpha \) for the lignite has a sharp increase at low temperatures due to CO, related crosslinking. This can be seen by the appearance of CO, related bonds in Fig. 4d. These bonds are a significant fraction of the total bonds connecting the network. With this large number of additional bonds, the value of \( \alpha \) never achieves the critical value \( \alpha_c = 0.95 \) and the solid fraction of the coal remains too high to liquefy. On the other hand, \( \alpha \) for the bituminous coal is not increased by CO, related crosslinking. The value of \( \alpha \) falls below the critical value and sufficient liquid fraction is produced for the network to disintegrate and become fluid.

The viscosity model used here has terms that depend on the coal liquid temperature, the weight average molecular weight of the liquid fraction, and the volume fraction of solids, with an inhomogeneous gel-point. It is the last two factors which are most important.

In common with previous studies of coal viscosity a two-phase model is used. The particular equation chosen is that put forward by Mooney (17,32)

\[
\ln \left( \frac{\eta}{\eta_{\text{in}}} \right) = \frac{k_\varepsilon \phi_c}{1 - \phi_c/\phi_i} \tag{1}
\]

where \( \eta \) is the viscosity of the suspension, \( \eta_{\text{in}} \) the viscosity of the liquid, \( k_\varepsilon \) is the Einstein coefficient, and \( \phi_c \) is the volume fraction of solids, having a critical value \( \phi_i \) at which \( \eta \) goes to \( \infty \). Values of the constants are listed below.

Based on the model by Bartels et al. (27), the viscosity of the liquid phase is given by

\[
\eta_{\text{in}} = C \exp \left( \frac{E_a}{RT^*} \right) \exp \left( \frac{M_w/M_\varepsilon}{M_\varepsilon} \right) \tag{2}
\]

which on combining with Eq. 1 leads to
The constants used in the viscosity theory are as follows:

C: proportionality constant, \( C = 1.0 \times 10^{-4} \) Poise

\( k_e \): Einstein coefficient, \( k_e = 5.0 \)

\( E_a \): Activation energy for viscosity, \( E_a = 8 \times 10^6 \) kcal/mole

\( M_w \): Molecular weight parameter, \( M_w = 1000 \)

\( \phi_c \): Volume fraction of the solid phase at the gel-point, \( \phi_c = 0.7 \)

\( M_e \): Weight average molecular weight of the liquid

\( T^* \): Absolute temperature, cut-off at 708 K

\[ \eta = C \exp \left( \frac{E_a}{RT^*} \right) \exp \left( \frac{M_w}{M_e} \right) \exp \left( \frac{k_e \phi_c}{1 - \phi_c/\phi_c} \right) \]  

(3)

The value of \( k_e = 5 \) was arrived at empirically, i.e., to fit the data. This value, however, matches the situation in which liquid is entrapped within large agglomerates of solid (54). The value of the activation energies for coal was chosen based on measured liquid viscosities (from \( 5 \times 10^4 \) to \( 10 \times 10^4 \) kcal/mole) determined by Waters (55). Waters also showed that coal liquid behaves as a Newtonian fluid at strain rates encountered in standard viscosity measurements. The use of a cut-off temperature was introduced by Nazem (28).

RESULTS

There are two aspects to validating the model by comparison with data. The first is that the FG-DVC model should provide good predictions for pyrolysis products; the second is the comparison of predictions to fluidity data. Extensive comparisons of the FG and FG-DVC models have been made by Solomon et al. (39,40,42,43) and Serio et al. (41,53). These comparisons show good agreement between theory and experiment using rank independent kinetics for the Argonne coals and several other coals. An example of the fit of methane evolution for pyrolysis at 30°C/min for several coals used in this study is presented in Fig. 5. There are some differences between the predicted and observed evolution curves (the observed evolution in high rank coals is slightly slower than predicted), but in general the agreement is good.

All the viscosity data were fitted using the same viscosity equations and same constants. The only variable was the kinetic rate for bond breaking and crosslinking. When fitting the viscosity data, it was found that the slight differences in methane evolution (which is related to moderate temperature crosslinking) and in tar evolution (which is related to the bond breaking rates) adversely affected the viscosity prediction. For the viscosity results, the bond breaking and methane rates were adjusted to match the slow heating rate evolution curves. An example of the new predictions for the Upper Freeport coal is presented in Fig. 6. The new rates are presented in Table I. One additional change was made in the FG-DVC model to better match the fluidity data. This was to increase the crosslinking efficiency for methane from 1 to 1.5 crosslinks formed per methane evolved. This improved the fits to the fluidity data and can be justified on the basis that the evolution of gases formed from other peripheral groups (ethane, propane, etc.) may also lead to crosslinking.

The first example of the application of the model to predict fluidity is shown in Fig. 7. The data is from Oxley and Pitt (47) obtained by heating during an 11 minute period to constant temperatures of 400, 420, and 440°C. The coal is believed to be similar to the Upper Freeport. The agreement is excellent in following the increase and decrease in fluidity due to bond breaking and crosslinking, and in fitting the two orders of magnitude change in fluidity over a 40°C change in temperature.

Results for a higher rank coal studied by van Krevelen at constant heating rates are presented in Fig. 8a. The coal composition picked to represent the coal was that of the Pocahontas. However, the fluidity maximum for the coal is lower than expected based on the weight loss curve for Pocahontas. The bond breaking rate for this coal was, therefore, picked to be higher than we would expect for the Pocahontas coal. The theoretical predictions in Fig. 8b are in excellent agreement with the data.
Results for a Pittsburgh Seam coal obtained at high heating rates by Fong et al. (15) are presented in Fig. 9 as the symbols. The theory is shown as the lines. There is good agreement between theory and experiment for the onset of fluidity and for the maximum fluidity. The loss of fluidity is, however, predicted to occur much sooner than expected. The extract yield obtained by Fong et al. (15) in a heated grid experiment is also shown as a dashed line. The disappearance of fluidity predicted by our model does, however, appear to coincide with the disappearance of the extract yield. This is as expected since the model is dependent on the liquid fraction. The fact that the fluidity and extract data do not agree, may suggest that there are differences in temperature between the two apparatuses.

A number of additional comparisons were made between theory and experiments. A summary of the predicted and measured maximum fluidities for all the cases is presented in Fig. 10. There is good agreement over a fluidity range of five orders of magnitude and a temperature range of several hundred degrees.

CONCLUSION

1) A model for fluidity of coal has been developed based on a macromolecular network concept.

2) The network model is used to predict the fraction of liquids and the average molecular weight of the liquids under the combined effects of bond breaking and crosslinking.

3) The empirical model for an inhomogeneous melt assumes the fluidity to depend on the liquid fraction in the melt, on the viscosity of the fluid and on the temperature.

4) Good agreement is obtained with data for four coals which covers five orders of magnitude in fluidity and several hundred degrees in temperature. This agreement is obtained with fixed parameters in the empirical fluidity equations but with adjustments of the bond breaking and crosslinking rates to better fit the pyrolysis product yields.

5) At this stage of the development, we have a model which works for a variety of data, but is not necessarily unique. Emphasis is currently being placed on extending the range of applicability and on optimizing the model assumptions and constants.

ACKNOWLEDGEMENT

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REFERENCES

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50. ASTM D 2639-74 (reapproved, 1980).
<table>
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<tr>
<th>EXPERIMENTS:</th>
<th>FITZGERALD</th>
<th>FONG</th>
<th>OXLEY &amp; PITT</th>
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<tr>
<td>C %</td>
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<th>PITTS NO. 8</th>
<th>UPPER FREEPORT</th>
<th>POCAHONTAS Composition†</th>
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</thead>
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<td>19.5%</td>
</tr>
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<td>85.8</td>
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<td>60000</td>
<td>62000</td>
<td>63000</td>
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N/A: Not Available

*Based on fluidity data, the van Krevelen coal (24% volatile) appears to have kinetic rates comparable to the 90% carbon coals in Fig. 2 rather than the Pocahontas coal. For this reason the kinetic rates in the Table are higher than expected for Pocahontas.*
Figure 1. Apparent Fluidity as a Function of Time at 407°C for a Typical Coking Coal (34.4 percent dry ash free volatile matter, coal rank code number 401b). From Ref. 48.

Figure 2. Rate of Devolatilization at a Constant Heating Rate of 3.0°C/min. a) Data of van Krevelen (1), b) Data for Argonne Premium Samples.

Figure 3. Representation of a Coal Molecular Network in a Monte Carlo Simulation (a and c) and Corresponding Molecular Weight Distribution (b and d). In the Molecule, the Circles Represent Monomers (ring clusters with their peripheral groups). The Molecular Weight Distributions of the Network are Shown as Histograms in b and d. The Histogram is Divided into Tar, Pyridine-Soluble and Pyridine-Insoluble Fractions. The Area Under the Histogram Corresponds to the Weight Percent of the Oligomers.
Figure 4. Comparison of the Variation in the Unbroken Bond Concentration, Bonds/Cluster, \( \alpha \) and Liquid Fraction with Time at Constant Temperature of 440°C for a-c) Upper Freeport Bituminous Coal and d-f) Zap Lignite. Unbreakable Bridges; Labile Bridges; CH\(_4\) Related Crosslinks; CO\(_2\) Related Crosslinks; Initial Crosslinks.

Figure 5. The Evolution of Methane from Argonne Premium Samples in a TG-FTIR at a Constant Heating Rate of 30°C/min (53). Solid Line is Data, Dashed Line is Theory. The Temperature History is shown on the Pocahontas Plot.
Figure 6. Comparison of Theory with TG-FTIR Experiment on Upper Freeport Coal for the Evolution of a) Tar plus Aliphatic and b) Methane Using the Improved Rates shown in Table 1.

Figure 7. Comparison of Experiment and Theory for Fluidity of a High Rank Coal at Constant Temperatures of a) 400°C, b) 420°C and c) 440°C. The Experiment is for a Coal which has 30% Volatile Matter Content (47) and Theory is for Upper Freeport Coal.

Figure 8. Fluidity at Constant Heating Rate. a) Experiment Data of Van Krevelen (1) for 24% Volatile Coal and b) Theory for Pocahontas Coal Composition (see note in Table 1).
Figure 9. Viscosity at High Temperatures. Symbols are Data of Fong et al. (15).

Figure 10. Maximum Fluidity for Four Experiments.
THE PLASTOFROST TECHNIQUE FOR STUDYING
THE CARBONIZATION OF COAL - A RE-EXAMINATION

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Introduction

The Plastofrost technique was developed by Ritter and Juranek[2] in West Germany to observe the coal-to-coke transformation (softening, pore development and recrystallization), and the interaction of coal macerals at different degrees of carbonization. Changes occurring at different temperatures during the process become visible and if captured on film, produce a time-temperature record of the carbonization stages. Although hailed as a useful technique by researchers the Plastofrost technique enjoyed just a brief period of popularity. Since the 1960's the technique does not appear to have been mentioned in the coal science literature. A recent thesis[3] seems to have rekindled interest in the method.

Our objectives in this paper are to describe the Plastofrost technique and the modifications we have made, illustrate the information obtained, and to examine the range of scientific and technical questions this procedure can be used on.

The principle of the Plastofrost technique is to produce a temperature difference across a coal sample so that the bottom of the sample reaches at least 550°C when the top of the sample has not yet attained 350°C. The maximum temperature ensures that semicoke forms so that the coke texture can be observed, while limiting the top temperature permits dewatering to occur, but not softening. Placing thermocouples in the sample gives the temperature gradient; the temperature at each point in the sample is known and a temperature can be assigned to each visible stage of the coal to coke transformation. Heating of the sample is unidirectional just as in a coke oven. However, in the Plastofrost unit, the sample is heated from the bottom. It differs, therefore, from a coke oven in the direction of gas flow with respect to the temperature front. Some of the gas in a coke oven will move through the hot zone, and undergo further cracking, whereas in the Plastofrost, gas flow is only into the cooler region of the sample. The significance of this difference is not known. Nevertheless, movement of the temperature front through the sample makes the Plastofrost a better model of a coke oven than a dilatometer or a plastometer whose designs emphasize uniform heating.

Equipment

Figure 1 shows a schematic (elevation) of the Plastofrost apparatus as modified for the present study. The two main components are the furnace and the coking attachment. The furnace consists of a nickel-plated copper slab in which four 300 watt cartridge heaters are enclosed. A chromel/alumel thermocouple insulated with ceramic tubing placed 5 mm beneath the top surface of the slab measures the temperature (see Fig. 1). The bead of the TC is at the centre of the slab.

The coking attachment comprises a baseplate; a coking cylinder; and a ram. The coking cylinder has an inside diameter of 41 mm and a height of 75 mm. Wall thickness is 3 mm. The cylinder can be separated vertically into halves and has ten evenly spaced holes 5 mm centers, along each side of the vertical split. Ceramic tubes (2.5 mm o.d.) are placed in these holes, as shown in Figure 1, and chromel/alumel thermocouples are inserted so that the measuring junctions are located along the axis of the cylinder. Halves
of the cylinder are clamped together as shown in the figure.

The cylinder fits into an insert in the baseplate. This plate measures 110 mm x 110 mm and is 6 mm in thickness (Fig. 1). Three 6.3 mm rods, 115 mm in height, extend from the base plate to the retainer for the ram. The ram itself is 10 mm thick and has a diameter of 39.75 cm, just slightly less than the inside diameter of the coking cylinder so that it can easily compact and retain the coal within the cylinder. It is fitted with a 76.5 cm long "T-shaped" handle, threaded through the retainer. Thus the ram can be raised or lowered to provide any desired degree of compaction in the coal.

The coking attachment is placed in a snug fitting inset on the top plate of the furnace. This is stepped as shown in the figure to reduce heat flow to the cylinder walls. The furnace provides unidirectional heating to the sample in the cylinder from the bottom upwards.

A microcomputer based control and data acquisition system is required to monitor the 10 thermocouples in the sample and to control the furnace temperature. Details are given by Duever 65 and in a WCPD report 66.

Procedure

Prior to loading, an aluminum foil was placed in the coking cylinder and ceramic tubes, 5 cm in length, were fitted in to the holes located in the coking cylinder. The cylinder was placed on the baseplate before coal was added. A sample of air dried, ground coal, weighing 85 grams, was incrementally packed into the cylinder using the ram to guarantee a constant packing density of 0.9 g/cm³ for all samples. The attachment was then suitably insulated using fibrefax and insulating tape. Insulation was needed to ensure a uniform radial temperature distribution. The ten chromel/alumel thermocouples were inserted into the ceramic tubes and connected to a junction strip as the last step. In some experiments, only 66.5 g of coal were used to give a density of 0.76 g/cm³.

The samples were heated in air until the temperature in the lowest level of the coal reached 200°C. At that time nitrogen was introduced into the test chamber to prevent oxidation at the sample. The furnace was heated thereafter at the maximum heating rate until its temperature reached 400°C. The temperature in the lowest level of the packed coal sample at this time was usually about 250°C. Above 400°C the furnace heating rate was controlled at 3°C/min. Heating continued until the temperature in the lowest level of the coal reached about 550°C. At this time, the furnace was turned off, the coking apparatus removed from the furnace plate left to cool in an inert atmosphere until the temperature at all levels fell below 200°C. At this point, the foil wrapped sample was impregnated using a polyester resin sometimes thinned with acetone. After hardening the sample was cut into two pieces perpendicular to the ceramic tubes using a diamond-tipped circular saw. Each half was impregnated with polyester resin again, but this time under vacuum.

The final step in sample preparation was grinding and polishing. The former followed the recommendations of the Bituminous Coal Research Inc. 67 The exposed face of the coked samples were polished to produce scratch-free surfaces suitable for microscopic examination using three polishing stages, each of three minutes duration. After each polishing stage, an ultrasonic cleaner was used to remove all polishing or grinding particles. Using a Zeiss UNIVERSAL Research Microscope, Plastofrost samples were examined by reflected light using parallel polars and a 1/4 λ plate inserted between the specimen surface and the analyzer to characterize the samples in terms of their optical texture. A strip 5 mm wide on either side of the center axis of the cylinder was examined. Juránek et al. 68 measured the temperature profile perpendicular to the center axis and found that within such a strip, deviation from the temperature along the center axis was within 3°C.
The first step in the microscopic evaluation was to determine the relative positions of the ceramic tubes making use of a stage micrometer. These tubes held the thermocouples during the tests so that the exact temperatures at these positions were known. Then samples were examined at 50X magnification in air to observe the softening characteristics of the coal, its resolidification, and the nature of the coke formed. This was accomplished by identifying the following transitions found by Ritter and Juranek (12) and Juranek (13) to be common to coking goals.

1) The first appearance of pores in the individual grains.
2) The initial fusion of the grains.
3) The point at which there is a significant increase in the proportion of pores.
4) The completion of fusion where individual grains are no longer distinguishable.
5) The development of anisotropic semicoke.

With the aid of the stage micrometer, positions could be assigned to each of these changes to the nearest tenth of a millimeter and the temperatures for each transition could be estimated from the temperature record.

Completion of fusion and a significant increase in pores are relatively gross characteristics and could easily be identified at 50X magnification. Determinations of initial pore development and grain fusion were more difficult and generally required higher magnifications of 100 and 200X. The anisotropic nature of the semicoke was observed at 200 and 500X magnification. The development of anisotropy in the softened coal mass is an indication of decreasing viscosity. With increasing time and temperature, anisotropic domains grow and may form large regions of uniform orientation. Thus since these domains should not change above the resolidification point, the point at which domains cease to grow and change should be the resolidification temperature.

Further details of procedure are available (13). Several experiments were performed using coal-bitumen slurries. A different procedure had to be developed to prepare samples from slurries. Fluidity of the surry during heating was a problem. A paper at recent ACS Symposium (17) discusses the procedure developed. An extended discussion appears in a report in the public domain (15).

**Plastotrast Observations**

As mentioned above, some of the carbonization stages are easily identified. One of these is the completion of fusion. Figure 2 shows the observed completion of fusion in a cretaceous LVB sample. The black and dark grey regions are unfilld and resin filled pores or interparticle voids respectively while the light grey, largely featureless region is the fused vitrinite. Boundaries between bordering vitrinite macerals have disappeared and bridges connect well separated macerals. Devolatilization pores are the irregular sized, semicircular regions in the vitrinite macerals. A distinct inertite maceral, probably semi fusinite, is at the lower left border of the photo. Stress cracks arising during cooling are also visible.

Use of 1/4 λ plate with parallel polarizers permits the texture of the cooled molten phase and the semi coke to be observed. Figure 3 shows the texture of the anisotropy for 3 samples. Magnification of all samples is 200X. The uppermost figure shows elongated, flow domain texture at 458°C that is typical of both carboniferous and cretaceous LVB coals. Texture has been interpreted by Grint et al. (14). Surprising is that this anisotropy is seen at a temperature 25°C below the temperature of maximum dilatation measured using a Ruhr dilatometer for the coal (14). The coal must still be fluid at this temperature. Thus, the texture represents either structure in the softened or molten coal or formed as the coal solidifies on cooling in the sample preparation procedure. Appearance of anisotropy prior to the temperature of maximum dilatation, that is, while the coal was still plastic, occurred with both cretaceous and carboniferous MVB coals. It did not occur with the HVB samples.
For these coals, the temperature of maximum dilatation coincided with the temperature of the first appearance of anisotropy so that the latter temperature does signal semicoke formation for this rank of coal.

Coal rank (vitrinoid mean reflectance) affects texture of the semicoke strongly. Figure 3b shows well developed fine mosaic anisotropy surrounding a pore in the lower right of the photomicrograph. The vitrinoid material seems tightly bonded to the unsoftened and unfused semi fusinite that appears in the upper part of the photomicrograph. The coal used for this sample was a cretaceous HVB which had a reduced vitrinite content. The fine to coarse grain texture is typical for the HVB coals. The temperature reached at the point where the photomicrograph was taken was 550°C. The texture seen in Fig. 3b contrasts well with the texture for an LVB sample shown in Figure 3c.

Figure 3c is taken from another, as yet unpublished study of coal carbonization during co-processing of bitumen and coal (10). The circular black region is a resin filled devolatilization pore surrounded by bitumen semicoke. Fused vitrinite is the bright region with very little texture. The photomicrograph suggests that neither the bitumen or the plastic coal are mutually soluble and the presence of bitumen does not interfere strongly with the fusion of vitrinite macerals.

Plastofrost Applications

The brief discussion of the photomicrograph indicates some of the applications of the Plastofrost technique: development of anisotropic texture as carbonization proceeds; measurement of the softening temperature, the plastic range and, for HVB coals, the resolidification temperature; and pore size, distribution and wall thickness. Beginning with Duever’s study (10), the Waterloo Coal Research laboratory has applied the Plastofrost to three problems: 1) measuring the effect of metal salts on coal particle fusion during bitumen coal co-processing, 2) assessing the accuracy of the dilatometric plastic range, and 3) exploration of the failure of rheological tests to predict the good coking performance of North American cretaceous coals.

In the first of the above three applications (10), two cretaceous and two carboniferous coals were used along with a heavy bitumen (vacuum bottoms). Plastofrost samples were prepared from the coals with 0, 5 and 20 wt% metal salts, the vacuum bottoms, and slurries of 30 wt% coal in the vacuum bottoms with metal salt levels of 0, 5 and 20 wt%. It was found that the salt delayed initial fusion of the coal grains and completion of fusion. The anisotropic texture of the semicoke was diminished by the salt. The presence of vacuum bottoms suppressed coal fusion, probably by physically separating the coal grains. Fusion is also slightly suppressed at 20 wt% additive; 5 wt% seemed to have little effect. Dissolution of vitrinite in the bitumen was not observed. The coal and vacuum bottom phases carbonize separately yielding distinct, but well bonded semicoke. Anisotropic texture of the vacuum bottoms coke is strongly diminished by the presence of the finely ground coal. The micrographs suggest that the metal salt impregnated coals expel the salt on softening. This salt collects on the maceral surfaces and may physically interfere with the fusion process.

The second and third applications employed the same Plastofrost data taken with two suites of HVB to LVB coals of the carboniferous and cretaceous eras. The coals were split by gravimetric means into vitrinite enriched and depleted samples. In our study of dilatometry plastic ranges (11), it was found that the plastic range agrees well with the range obtained from the Plastofrost initial softening and first appearance of anisotropy temperatures for coals showing positive total dilatations and HVB coals with high vitrinite content. This is shown in Figure 4. With the exception of several HVB coals, the dilatometer seriously underestimates the plastic range of poorly or non-dilatating coals. The explanation
for this is that dilatometry does not correctly measure the softening temperature of many
coals. Only with HVB coals do the estimates of initial softening temperature by the two
techniques agree.

As discussed earlier, the Plastofrost estimate of the resolidification temperature
(semicoke formation) is incorrect for MVB and LVB coals. Thus, that technique does not
give the ‘real’ plastic range. The best estimate seems to come from using the Plastofrost
measurement of the initial fusion temperature and the dilatometer reading of the
temperature of maximum dilatation.

The third Plastofrost application [6] investigated the observation [12,13] that rheological
tests on certain bituminous coals of cretaceous origin indicate that the coals have poor
coking quality even though commercial use and ASTM Sole Heated Oven tests show that
these coals produce good quality coke. The Plastofrost observations indicate cretaceous
bituminous coals exhibit all the carbonization stages seen in good coking coals.
Temperatures of the carbonization stages do not differ greatly between the carboniferous
and cretaceous coals as well. The plastic range of the latter coals is generally smaller for
the LVB coals; the difference approaches 55°C. It was concluded that the problem with
the rheological tests lies with the assumption that contraction and dilatation depend only
on fluidity of the coal. These changes probably reflect the viscosity of the softening coal
and the size and distribution of the inert macerals in the coal.

Three years experience with the Plastofrost technique indicate measurements are
reproducible, provided the same observer makes the readings. However, sample
preparation is slow and measurements have a subjective element because different
observers obtain different stage temperatures from the same sample.

Acknowledgements

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Waterloo Centre for Process Development. Dr. J.T. Price of CANMET was the supervising
scientist on these contracts. His active participation was very much appreciated.

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Figure 1 Schematic of the Plastofrost Apparatus
Figure 2  Completion of fusion (413°C) for a vitrinite enriched cretaceous LVB coal

(a) Flow domain anisotropy in a LVB Semicoke
Figure 4 Cross plot of dilatometric and Plastofrost plastic ranges
INVESTIGATIONS OF THE ROLE OF COAL THERMOPLASTIC PROPERTIES AND COKE STRUCTURE IN GASIFICATION PROCESSES

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London SW6 2AD
UK

INTRODUCTION

Coal classification schemes have been developed over many years from studies of the physical and chemical properties of coals as a method of dividing coals into various categories according to their behaviour during carbonisation and combustion. Although there is no universally accepted scheme, most coal classification schemes are based on two main types of parameters: a) volatile matter, and b) caking and swelling properties. The limited scope and empirical nature of the techniques used in classification schemes and their variation with experimental conditions means that classification schemes have only limited applicability when comparing coal behaviour in high pressure gasifiers where the nature of the process is a primary consideration and the experimental conditions are vastly different from those used in the tests.

The thermoplastic properties of coal, as well as characterising the initial agglomeration processes, are important in determining both porous structure and carbon texture of the coke product. Both the coal and coke structures are significant factors in determining gasification behaviour. The coke strength and reactivity during gasification are of considerable significance in fixed bed gasifiers. The agglomerated coke is broken up by the stirrer to facilitate the countercurrent flow of gases and solids (1) and hence, the mechanical strength of the coke may be an important factor. In the case of weak cokes, a wide size range may be produced and increased levels of dust may occur causing a loss of efficiency and throughput. Coke structure is important in determining reactivity towards oxidising gases which is a main gasification step.

The objective of this study is to provide information on the dependence of coal and coke properties under experimental conditions found in fixed bed gasifiers. The direct link between measurements of coal thermoplasticity and coke structure obtained by examining the structure of the carbonised residues from the high pressure thermoplasticity measurements is considered to be an important aspect of the investigation since it eliminates any possible ambiguities in comparing various sets of data. From these considerations and other experiments under simulated gasifier conditions, comparisons with gasifier operational data can be made which should make it possible to develop optimum methods for predicting coal performance in a particular process.
EXPERIMENTAL

The coals used in this study were a strongly caking coal (Coal Oa, NCB Classification Scheme 301a) and a moderately caking coal (Coal H1, NCB Classification 602) with the characteristics given in Table 1.

The high pressure dilatometer used in this study has been described in detail elsewhere (2). It operates at fixed pressures up to 10 MPa and heating rates up to 60°C min⁻¹. In all other respects, the dilatometer geometry and sample preparation were standard (BS 1016: Part 12) with the exception of the preliminary temperature stabilisation which was not used with heating rates above 30°C min⁻¹. The standard deviations of the contraction and dilatation values are estimated to be 5-10% and 10-15% respectively.

The high pressure plastometer used in this investigation has a geometry which is a scaled down version (x50%) of the Brabender Plastometer which has been described previously (3). It operates at fixed pressure up to 10 MPa, heating rates up to 40°C min⁻¹ and rotational speeds in the range 2-30 revs per minute. A rotational speed of 10 revs per minute and a sample weight of 12.5 g (particle size fraction 0.5-1.0 mm) were used in all experiments.

The carbonised residues from the high pressure dilatometer and plastometer (HTT 550°C, Soak Time 0.1 hour) were crushed, mixed with epoxy resin and mounted in the form of discs. These discs were ground and polished. The polished blocks were examined by polarised light microscopy with an X 50 objective at an overall magnification of X 500 with the polars adjusted close to extinction. The different structural features were classified according to their appearance, size and shape, in terms of mosaic anisotropy of various grain size, flow type anisotropy and isotropic material. A 300 point count was used for quantitative measurements on each sample. The error in these measurements is estimated to be better than ±5%. The Optical Anisotropy Index (OAI) was calculated according to the equation described previously (4,5) which is given below.

\[ \text{OAI} = 1\text{f} + 2\text{fm} + 3\text{cm} + 4\text{c} + 5\text{gf} + 6\text{f} + 7\text{b} \]

where f=fine mosaic, m=medium mosaic, c=coarse mosaic, gf=granular flow, f=flow and b=basic anisotropy.

RESULTS AND DISCUSSION

Figure 1 shows a comparison of the plastometry results obtained for Coal H1 with a heating rate of 30°C min⁻¹ at pressures of 0.5 and 5 MPa. It is clear that a change in pressure has modified the plastometry characteristics. For this particular coal increasing pressure causes a decrease in the coking intensity while the caking intensity remains virtually unchanged. It is interesting to note that the onset of caking is sharper at lower pressure with the initial softening temperature decreasing markedly with increase in pressure. The plastic range also increases correspondingly with increase in pressure. A graph of plastometry parameters against pressure is shown in Figure 2. This clearly illustrates the different behaviour of the caking
and coking intensities with respect to pressure. In contrast, the plastometry parameters of coal Oa show similar trends with the exception of the coking intensity which does not change markedly with changes in pressure. The effect of heating rate on the plastometry characteristics of both coals is quite marked. The plastometry curves show that the caking intensity for both coals is not affected greatly by changes in the heating rate and this is similar to the effect of changes in carbonisation pressure. Figure 3 shows that both the coking and maximum fluidity intensities decrease dramatically with increasing heating rate. The apparent plastic range also increases with heating rate.

To understand the changes in plastometry characteristics, the swelling during carbonisation needs to be considered. Previous work has shown (2,4-8) that the swelling characteristics of coals are markedly dependent on heating rate and pressure, and cannot be predicted accurately from their swelling under standard conditions (atmospheric pressure and low heating rate). The three types of dilatation behaviour with respect to pressure which have been observed, depend to some extent on coal rank and are as follows:

a) an increase in dilatation with pressure;
b) an increase to a maximum at 1-1.5MPa followed by a decrease; and
c) a decrease in dilatation with pressure.

In contrast, the dilatation of coals as measured by the method used in this study, increases with increasing heating rate. A limiting value of the dilatation was observed at a heating rate of 20°Cmin⁻¹ in a previous study (4). An increase in pressure will have two main effects: a) a reduction in the volume of gas trapped in the fluid phase which would tend to decrease the swelling; and b) an increase in the secondary reactions by decreasing the volatility of tar and increasing the residence time in the fluid phase which would tend to increase dilatation. The changes in dilatation behaviour can be rationalised by considering the balance between the release of gaseous and liquid volatiles. The variation of the dilatation of coal Oa with heating rate at 2MPa pressure is shown in Figure 4. The dilatation of coal Oa increases with heating rate but decreases with increase in pressure (0.5-5MPa). A graph of dilatation against plastometry torque parameters for a range of heating rates (3-20°Cmin⁻¹) with a carbonisation pressure of 2MPa is shown in Figure 5. This graph clearly shows that there is a correlation between some of the plastometry and dilatometry parameters. It is noticeable that the caking intensity is not as sensitive to changes in dilatation as the coking and maximum fluidity intensities which change significantly.

Investigations of the optical anisotropic content of cokes derived from a wide range of coals have shown that it is a useful parameter for characterising their structure. Previous work has shown (4,5,9) that changes in carbonisation pressure and heating rate can have a considerable effect on the optical anisotropic
In particular, the anisotropic content of cokes usually increases substantially with pressure at heating rates of \(40^\circ\text{C/min}^{-1}\) to a limiting value above approximately 3MPa. The corresponding increase in anisotropic content appears to be much smaller at low heating rates. However, there is only a limited amount of information available in the literature on this aspect. In general, the change in OAI development in relation to pressure varies with rank in a fairly systematic manner but there is no direct correlation between individual rank and anisotropy parameters. The results suggested that the OAI changes are related to the influence of pressure on the retention of plastic material and modification of the plastic range. The variation of optical anisotropy index (OAI) for cokes derived from coal Oa at a carbonisation pressure of 2MPa with heating rate is shown in Figure 6. It is apparent that the OAI increases with increasing heating rate. For this particular coal, the changes in OAI also correlate with some of the plastometry parameters, in particular, the coking intensity, the intensity at the point of maximum fluidity and the plastic range. Further work is needed on a wide range of coals to establish definitive correlations between plastometry parameters, swelling characteristics and coke porosity and structure.

**CONCLUSIONS**

The relationship between coal thermoplastic properties and coke structure is very complex. The results of this investigation have shown that these properties are strongly dependent on the experimental conditions and, in particular:

- a) increased swelling is accompanied by a decreased plastometry coking intensity.
- b) The plastometry caking intensity is considerably less sensitive to change in experimental conditions than the other plastometry parameters.
- c) The optical anisotropy index is increased by heating rate and this is accompanied by changes in plastic range, plastometry coking intensity and a decrease in the apparent viscosity at the point of maximum fluidity.

These changes can be rationalised by considering the release of gaseous and liquid volatiles during the carbonisation of the coal. The lack of sensitivity of the caking intensity to heating rate and pressure is consistent with its origin being partly softening prior to the major decomposition. Further work is needed to relate coal thermoplasticity measurements to other coke structural data, in particular, texture and porosity measurements.

**REFERENCES**


Table 1
Characterisation Data for the Coals used in this Study

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<td>23</td>
<td>30</td>
</tr>
<tr>
<td>Plastic Range(°C)</td>
<td>87</td>
<td>73</td>
</tr>
<tr>
<td><strong>Gieseler Plastometry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max.Fluidity(ddpm)</td>
<td>590</td>
<td>535</td>
</tr>
<tr>
<td>T1 - T2 (°C)</td>
<td>91</td>
<td>69</td>
</tr>
<tr>
<td><strong>Petrographic Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reflectance(%)</td>
<td>1.46</td>
<td>0.71</td>
</tr>
<tr>
<td><strong>Maceral Analysis (vol.%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitrinite</td>
<td>65</td>
<td>78</td>
</tr>
<tr>
<td>Exinite</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Inertinite</td>
<td>35</td>
<td>13</td>
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Fig. 1. A comparison of the plastometry curves for coal H1 at 0.5 and 5 MPa (heating rate 3°C min⁻¹).

Fig. 2. The variation of plastometry torque parameters with pressure for Coal H1 (Heating Rate 3°C min⁻¹).
Fig. 3. The variation of plastometry torque parameters with heating rate for coal H1 (Pressure 2 MPa)

Fig. 4. The effect of heating rate on the dilatation of coal Oa (Gauge pressure - 2 MPa)
Fig. 5. The variation of dilatation with plastometry torque parameters at 2 MPa pressure for coal Oa.

Fig. 6. The variation of optical anisotropy index (OAI) with heating rate for coal Oa (Pressure 2 MPa).
THE EFFECTS OF OXIDATION AND WEATHERING ON
COAL COMBUSTION

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INTRODUCTION

General Review of Coal Oxidation

The low temperature oxidation of coal dramatically influences and alters inherent properties. The deleterious effect that oxidation has upon the coking and caking properties of coals, through the loss of plasticity and fluidity, is well documented [1,2,3]. The oxidative mechanism and processes by which coal properties are affected are discussed at length in the literature. Putnam et al [4], examining a suite of naturally weathered coals, discuss the possible transformation of aromatic compounds within the extractable organic material into molecules containing polar substituents. Larsen et al [2] suggest that the plasticity and fluidity of vitrinite rich coals can be lost by the oxidation of reactive benzylic positions and their replacement by carbonyl and carboxyl functional groups, with the concomitant loss of donatable hydrogen from the coal structure. In addition, an increase in cross-link density, due to the introduction of oxygen-bearing functional groups into the macromolecular structure of the coal, may prevent depolymerisation and plasticity during char formation.

Coal Oxidation Related to Combustion

Nandi et al [5], in their investigation into the role of inert coal macerals in pulverised fuel combustion, determined that the combustion efficiencies of coal were inversely related to the (organically) inert content of the coal feedstock during pilot-scale combustion experiments. Included in their category of organically inert material were what they considered to be oxidised vitrinite. Axelsson et al [6], investigating the effects of oxidation upon in-situ outcroppings and stockpiled coal, discuss the problems encountered when attempting to characterise oxidised coal using conventional techniques, noting the additional complicating factors petrographic composition has upon techniques such as Free Swelling Index. They concur with earlier studies [2] that postulated different mechanisms for oxidation to occur above and below 80°C. However, few studies discuss the effect that the oxidation of pulverised-coal feedstock has upon pyrolysis and combustion using Entrained Flow Reactor (EFR) apparatus. With increasing world coal trade that often requires the temporary stockpiling of coal, either prior to, or subsequent to, shipment to various points of usage, the effects of oxidation upon coal feedstock require some attention. There are no grounds for assuming that the specifications quoted by the coal vendor or that the published characteristics of commercial steam coal are fixed and remain constant in time.

OBJECTIVES

The overall objective of this study is to investigate the effect of oxidation upon the pyrolysis and combustion of pulverised coal feedstock using laboratory based equipment. More specifically the study aims to:

1. Investigate the effect of artificial oxidation upon the intermediate char morphology of pulverised fuel.
2. Investigate the effect of natural weathering upon the intermediate char morphology of pulverised fuel.
3. Assess the suitability of existing coal characterisation techniques when seeking to determine the effects of oxidation upon coal feedstock.
4. Suggest new ways of characterising oxidised coal feedstock.
EXPERIMENTAL

Materials Used

The three freshly mined Carboniferous bituminous coals used in this study were supplied by British Coal and originate from coal mines within the Northumbrian coalfield (UK). Coal 88/024 and 88/026 are both British Coal (1964) class 5Ws, whereas coal 88/025 is a class 700 (steam raising coal). Their characteristics are given in Table 1.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Rank</th>
<th>Ro max (ASTM) (%)</th>
<th>Maceral analyses</th>
<th>Proximate analyses (wt % dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>88/025</td>
<td>Hvb</td>
<td>0.73</td>
<td>61.2</td>
<td>39.0</td>
</tr>
<tr>
<td>88/026</td>
<td>Hvb A</td>
<td>0.79</td>
<td>76.4</td>
<td>35.0 10.02</td>
</tr>
<tr>
<td>88/024</td>
<td>Hvb A</td>
<td>0.93</td>
<td>72.2</td>
<td>37.0 5.1</td>
</tr>
</tbody>
</table>

Sample Preparation

The three freshly mined samples of coal were received in lump form (>10 cm⁻¹) within hours of being mined. They were crushed to (>2.5 mm) in a mechanical jaw crusher and each coal subdivided into twelve individual samples, representing two sets of six per coal. One set of five samples from each of the three coals was placed in a covered (lined) container and placed in the open air. The second set of five samples from each of the three coals was placed in a large heated roaster and oxidised at 100°C (±5) in static air. The sixth sample from each was analysed immediately and used as the datum sample. Samples of weathered and oxidised coal were removed periodically for analysis, thereby providing both artificially oxidised and 'weathered' samples.

Analytical Techniques

A Stanton Redcroft STA 780 TGA was used for all proximate analyses [7]. Calorific value determinations were obtained using a Gallenkamp Adiabatic bomb calorimeter. A Carlo Erba 1160 Carbon, Hydrogen and Nitrogen elemental analyser was used for the elemental analysis, oxygen was determined by difference. The Infra-red spectra of the coals were produced using a Nicolet 20SX Fourier-transform Infra-red spectrometer with the KBr pellet technique. Each spectra was generated using a total of 30 scans per sample.

Petrographic Analyses

All petrographic analyses of the coals were performed on a Leitz MPV3 microscope photometer. Vitrinite reflectance was determined using non-polarised light (½%Ro with random) on a crushed grain mounted block and based upon 100 measurements. The maceral analyses represent a total of 500 individual counts on grain mounted blocks, using a Swift point-counting device and interpoint and interline distances of 50 μm. Quantitative fluorescence microscopy on grain mounts of un-crushed coal was achieved using an HBO 100 mercury lamp, an EMI S20 photomultiplier tube (PMT), Plomdep, a Zeiss 'Plan Neofluar' x40 0.9n.a. triple-immersion objective (using water), a masked uranyl glass standard and the filter block combinations Tu and I2 (BP 450-490, RKP 510, LP 515). Fluorescence intensity measurements were conducted at 650 nm using a 20 μm measuring spot and the I2 filter block combination. A black cavity cell was used to compensate for parasitic reflections and for zeroing the photometer and calibration of the photometer was achieved using an uranyl glass in which the V.D.U. was set to read 100% [8]. Fluorescence intensity measurements scanned across coal particle surfaces was accomplished using an EMI S20 PMT supplemented by a Hamamatsu R446 PMT, which was attached via the camera tube on the microscope trinocular head. The EMI S20 PMT was used for the measurements conducted at 650 nm and the HTV R446 PMT was used for measurements conducted at 546 nm, thereby enabling simultaneous measurements at both wavelengths on the same field-of-view. The interpoint distance of 20 μm was achieved using a stepping stage set, with a procedure that involved examining the field-of-view using the Tu filter block, focusing, measuring the reflectance at 546 nm (%Rwater, n = 1.3 @ 23°C, ±2°C) using the stabilised tungsten lamp, switching over to the I2 filter block and opening the synchro-compur shutter, positioned in front of the mercury lamp, for the duration of the measurement (2 sec) at
A new measuring area was then selected using the stepping stage and the process repeated. Chars were produced from the coals (38 to 75 μm size fraction) in an Entrained Flow Reactor (EFR) (Figure 1.) in N₂ at 1273 ± 5K, consisting of a reaction tube of 1.66m in length using a gas flow rate of 38 l min⁻¹, to give laminar flow conditions and a residence time of 1 second. Char morphology was analysed in terms of type (from Cenospheres, through Network, to Solid types), depending upon the extent of vesiculation and the porosity of the char, using a Swift point-counter and the Leitz MPV3. The anisotropy of the char types was also recorded using a light microscope (x800 overall magnification) and a Swift point-counter. The internal porosity of each char was derived by Image Analysis using transmitted light on thin sections (5μm thick) of epoxy mounted char.

![Diagram of the EFR apparatus used in this study.](image)

Figure 1. A schematic diagram of the EFR apparatus used in this study.

**RESULTS and DISCUSSION**

**Proximate Analyses**

The proximate analyses of the oxidised coals show an initial rapid loss in their volatile matter content, as demonstrated in Figures 2 and 3, with a gradual decrease in the rate of loss as the duration of oxidation increased. For all coals, the rate of volatile matter loss is greater in the artificially oxidised series of coals than for the naturally oxidised coals over a similar period of time, although, in the case of the 88/024 weathered coal series the volatile matter content loss is less than coal series 88/025 and 88/026 over the same period of time reflecting the influence of rank. Despite initial differences in volatile matter content, reflecting the differences in petrographic composition (Table I.), weathered coals from the 88/025 and 88/026 series attain similar values after 19 weeks and decrease by the same amount over the two successive sampling points.
These observed trends are augmented by a similar decrease in elemental hydrogen and elemental carbon in preference to oxygen and by a decrease in the calorific content of the coal, as noted previously in a study discussed by Axelson et al [6].

Infra-red Analysis and Functional Groups

Infra-red investigations suggest that the main processes taking place involve the progressive removal of aliphatic hydrocarbons and the inclusion of oxygen bearing functionalities within the molecular structure of the coal. The removal of aliphatic hydrocarbons, such as \( \text{CH}_2 \) and \( \text{CH}_3 \), is indicated by a decrease in the absorption bands at 2920, 2850 and 1435 cm\(^{-1}\) and is accompanied by the development of absorption bands at 1620-1700 cm\(^{-1}\) (ketones), 1690-1718 cm\(^{-1}\) (carbonyls in acids), 1765 cm\(^{-1}\) (esters) and 1843 cm\(^{-1}\) (anhydrides) [9,10]. The development of ring-bound, conjugated, oxygen bearing functionalities is supported in this study by quantitative fluorescence microscopy.

Petrographic analysis of the coals

The vitrinite reflectance values (Figure 4.) increase to approximately 20 to 25% in the artificially oxidised coal series above those values derived from the fresh coals after a period of three months although the reflectance values determined upon the weathered coals decrease over the same period of time. This concurs with the work reported by Putnam et al [4]. The reflectance values determined in this study on oxidised and weathered coals represent measurements on crushed particles of varying size (>212μm) embedded within the grain mounted block. The findings within this study relating to the trends outlined for the artificially
oxidised coals concur with those of Prado [11] i.e. that the reflectance varies across the surface of a particle. Both Prado [11] and Cronauer et al. [12] comment on the absence of visible oxidation rims on low temperature artificially oxidised coals when using plain polarised light. Cronauer et al. [12], artificially oxidising coals under similar conditions to those reported here, considered the kinetics of low temperature oxidation to be diffusion controlled but failed to detect the presence of oxidation rims. They were, therefore, unable to verify their reaction concept. However, in this study, when observing the present series of low temperature artificially oxidised vitrinite coal particles in fluorescent mode, rims of low fluorescence activity (quenched fluorescence) as a direct consequence of oxidation for periods of up to one week, are clearly visible. Therefore, the development of conjugated oxygen bearing groups is supported by the observed quenching of fluorescence in oxidised coals. Ring-bound ketones, for example, have $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorbancies at 245 nm and 435 nm. The bond between the ketone and the aromatic group is associated with the $\pi \rightarrow \pi^*$ transition, whereas ketones give rise to the $n \rightarrow \pi^*$ transition. The electronic transitions of oxygen bearing groups increase in both wavelength and intensity with an increasing degree of conjugation. Fluorescence intensity measurements conducted at 650 nm across the polished surface of vitrinite particles (Figure 5) would appear to verify the oxidation kinetics postulated by Cronauer et al. [12], that the reaction appears to be predominantly diffusional at 100°C and under similar conditions. The rims of quenched fluorescence widen as the period of artificial low temperature oxidation increases, until eventually no measurable, or visible, fluorescence remains. However, in the case of the weathered coals no well defined oxidation rim exists in the vitrinite particles. Instead the fluorescence intensity diminishes gradually across the particle surface which would suggest that, under the conditions of weathering used in this study, the reactions are probably due to a combination of chemical control and diffusion.
Char morphology

The effects of low-temperature artificial oxidation upon the morphology of chars produced in the EFR are well illustrated by the coal series 88/024 (Figure 6) and the oxidised coal 88/025 series (Figure 7). Both unoxidised coals 88/024 and 88/025 are vitrinite rich (see Table 1.) and are of sufficient rank to produce a predominance of cenospheric char forms [Plate 1.].

Proportion of anisotropic char  92.4%  34.2%  2.2%  0%  0%  0%

Figure 6. EFR chars and the artificial oxidation of coal 88/024

Proportion of anisotropic char  46.2%  27.8%  1.4%  0.8%  0%  0%

Figure 7. EFR chars and the artificial oxidation of coal 88/025

The proportion of cenospheres produced during pyrolysis from the unoxidised coals and the percentage of char exhibiting visible anisotropy follows the rank dependence postulated previously [13]. However, the effects of artificial oxidation are most severe on the higher rank series 88/024. The decrease in the proportion of anisotropic char, from an original value of 92.4% down to 34.2% after oxidation at 100°C for one day, is notable. This is followed by a virtual elimination of all visible anisotropy in the chars after oxidation for one week. Furthermore, the systematic replacement of cenospheres by isotropic chars of a less-vesiculated nature, i.e. the tensi-network chars [Plate 2.], until the predominant char type is a dense and solid inertoid char type of low porosity [Plate 3.] as oxidation time increases (Figures 6 and 7) is a clear indication of the loss of thermoplastic properties during pyrolysis.
Deshpande et al [14] discuss the nature of molecular cross-linking and volatile evolution during the pyrolysis of coal in relation to the rank of the feedstock and the decomposition of carboxyl groups during pyrolysis. During the slow pyrolysis of a lignite (0.5°C s⁻¹), cross-linking starts to develop prior to the evolution of tar. At higher heating rates (2.0 x 10⁴ OCs⁻¹), cross-linking occurs simultaneously with tar evolution. Similarly, the thermoplasticity of a bituminous coal has been attributed to both the presence of cross-links in the macromolecular framework of the coal (vitrinite) and the behaviour of the "mobile phase" during pyrolysis [15]. Upon heating, the macromolecule decomposes and the coal exhibits visco-elastic properties allowing the aromatic units to slide over one another. The volatile matter, which is generated within the macromolecular framework, expands causing the viscous mass (proso-char) to expand during the simultaneous expulsion of gaseous material. The result is the production of a char, the morphology of which is largely dependent, according to the model of Spiro, upon the behaviour of the mobile phase during char formation.

Char formation cannot be readily explained by visco-properties alone. The formation of radicals is also significant during pyrolysis. The formation of radicals, which are highly reactive. Under the operating conditions of the E.F.R., and their probable stabilisation and transformation into volatile species, is possibly achieved primarily by hydrogen addition. The formation of the char particle is followed by the polymerisation and condensation reactions that occur during the recombination of non-volatile radical components. Therefore, the depletion of donatable hydrogen species through the oxidative replacement of reactive benzylic CH₃ or CH₂ groups possibly leads to a greater number of non-stable oxygen bearing radical components during pyrolysis. Solomon and Hasbun [16] formulated a 'functional group model', in which coal pyrolysis is regarded as a depolymerisation process that operates parallel to the decomposition of functional groups, in which the pyrolysis products compete for hydrogen-capping molecules for stabilisation. According to this model, the type and number of functional groups therefore control the kinetics and mechanisms that operate during pyrolysis.

There is some confusion in the literature [17] regarding the effects of oxidation on vitrinite reflectance. Such confusion exists because the oxidation of coal is dependent upon particle size and the temperature under which the gas-solid reaction takes place. In oxidative techniques that employ high temperatures, there is a 'reaction front', visible as a rim (heterogeneous gas-solid reaction), under low temperature conditions, such as natural weathering, there is no discernible reaction front and the oxygen appears to react progressively throughout the particle (homogeneous gas-solid reaction). Measurements conducted, with or without the central area of the particle beyond the gas-solid reaction front, will lead to variations in reflectivity not necessarily due to the chemical process of oxidation.

Bulk analytical techniques, such as proximate analysis, do not adequately predict the behaviour of oxidised pulverised fuel during pyrolysis or combustion. The techniques discussed above indicate values associated with coals of higher rank, although the behaviour of the oxidised coal during pyrolysis is more akin to low rank coals or coals containing a high proportion of the maceral inertinite. Therefore, careful monitoring of properties is necessary when stockpiling coal and the utilisation of petrographic techniques, such as fluorescence microscopy and the saffran-o staining technique [6] will help to discriminate between oxidised and unoxidised coals.

CONCLUSIONS

The progressive oxidation of coal feedstock severely alters the nature and morphology of the char produced during EFR pyrolysis. More specifically:

1. Artificial oxidation of the coal leads to a reduction in the porosity of the char, through a decrease in the extent of devolatilisation and a probable increase in the extent of cross-linking. Furthermore, there is a decrease in the anisotropy of the char as a result of oxidation.

2. The effect of weathering is similar to those witnessed by artificially oxidised coals, although the time required for comparable changes is much greater.

3. Existing coal characterisation techniques do not adequately assess the effect or extent of oxidation and some techniques, such as vitrinite reflectance, show variations not necessarily due to oxidation, but more to the experimental conditions (temperature) employed.

4. Petrographic techniques, such as fluorescence, are sensitive to the type and extent of oxidation and therefore represent a useful means of characterising oxidised coal feedstock.

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References:

ACKNOWLEDGEMENTS
S.L.B. thanks J. Pearson of British Coal for the samples of fresh coal.

Plate 1. Plate 2. Plate 3.
Transmitted light photomicrographs taken through thin sections of epoxy mounted char, showing the cross-sectional morphology and internal porosity due to variations in vesiculation and devolatilisation. Plate 1. shows a Crassicenosphere (thick-walled cenosphere): 68% porosity. Plate 2. shows a Tennunetwork char: 65% porosity. Plate 3. shows a Crassnetwork char (bottom left): 43% porosity; and an Inertoid, in which no vesiculation pores are visible although shrinkage cracks are visible: 15% porosity

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EFFECT OF OXIDATIVE WEATHERING ON ALIPHATIC STRUCTURE OF COAL

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ABSTRACT

Oxidative weathering of coal affects its structure and properties, and as a result, its utilization. For example, weathering adversely affects liquefaction yield, cokability, calorific value, and beneficiation. However, little is known about the chemistry of coal weathering. This paper discusses the effect of weathering on the aliphatic crosslinks that connect the aromatic-hydroaromatic units in coal. These crosslinks play a significant role in coal liquefaction and weathering alters them.

We have demonstrated, by acid-catalyzed transalkylation reactions and by GC-MS analysis of the products, that oxidative weathering reduces concentrations of several types of straight chain and branched chain aliphatic crosslinks. Infrared spectroscopic analysis shows that these crosslinks are converted to carbonyl and carboxyl groups. Plausible mechanisms for these transformations have been suggested.

INTRODUCTION

It is well known that oxidative weathering of coal induces irreversible structural changes that are detrimental to its utilization. For example, weathering decreases solvent extraction yields, coal liquefaction yield, and hydrocarbon yield during pyrolysis. It also reduces fluidity and calorific value, and causes poor coking behavior. Irreversible changes in surface properties, that in turn affect coal beneficiation, also occur during weathering. Effects of oxidative weathering on coal properties have been recently reviewed by Berkowitz and by Gray and Lowenhaupt.

Relatively little is known about the chemistry of coal weathering. It is known that the oxygen content of coal increases during weathering. The changes in structural features due to weathering have mostly been monitored by infrared spectroscopy. Painter et al. and Fuller et al. observed an increase in the carbonyl absorption with a simultaneous decrease in the C-H absorption region during weathering at 398° K and above. However, Martin and Chao found that during the weathering of Argonne Premium coal samples (73.0-85.6% C,daf) under ambient conditions the carbonyl absorption increases while the C-H absorption
in the aliphatic region remains unaffected. Liotta et al. found that the concentrations of ether and carboxylic acid groups increase upon prolonged ambient temperature weathering of Illinois #6 coal. Painter et al. also have noted formation of carbonyl and carboxylic acid groups with concurrent decrease in aliphatic C-H intensity during the initial stages of air oxidation of a highly coking Pennsylvania coal.

Our interest was to determine the fate of the aliphatic crosslinks during weathering. The aliphatic carbon structure, especially the crosslinks, play a significant role in coal liquefaction. The macromolecular network structure of bituminous and lower rank coals contains part of the aliphatic structure as methylene and polymethylene crosslinks connecting aromatic/hydroaromatic clusters. During liquefaction the relatively weak crosslinks undergo cleavage, while the hydroaromatic units provide part of the hydrogen for capping the free radicals produced by thermal decomposition. Therefore, the changes in aliphatic carbon distribution in coal during weathering can influence its liquefaction behavior.

There are as yet no accurate methods available for quantifying the aliphatic crosslinks in coal. Quantitative nature of the application of infrared (IR) spectroscopy is limited to certain general types of functional groups or bond types. Nuclear magnetic resonance spectroscopy, despite the success of dipolar dephasing techniques to decipher the extent of substitution on carbon atoms, is still inadequate to distinguish distinct structural entities.

In our studies, we have used acid-catalyzed transalkylation of coal using phenol and boron trifluoride, first reported by Heredy and Newworth, to quantify the aliphatic crosslinks in coals for monitoring changes in these crosslinks during weathering. It is assumed that during the transalkylation reaction, most of the methylene and polymethylene crosslinks are transferred to phenol. Since extensive solubilization is achieved by transalkylation, the information obtained from the analyses of the soluble products can provide useful information about coal structure. Although there are side reactions associated with the transalkylation reaction, we believe that it is adequate for comparing the relative features of raw and weathered coals. In addition to transalkylation, we have also used infrared studies to monitor the changes occurring during weathering.

EXPERIMENTAL

(a) Coal Samples. Three bituminous coals, namely, San Juan (New Mexico), Illinois #6, and Elkhorn (Kentucky) were used in the present study. Most of the studies were done on San Juan coal. The coals were collected from the freshly exposed mine faces. The samples were immediately transferred at the mine face to containers under a nitrogen atmosphere. The containers were closed tightly, sealed, and stored at approximately 273 °K. The grinding and sieving were done under a nitrogen atmosphere. The ground and riffled samples were kept in glass jars, sealed under nitrogen, and stored in a refrigerator at 277 °K. The proximate and ultimate analyses of the coal samples are given in Table 1.
(a) Weathering of Coal Samples. The coal samples, ground to -325 standard mesh, were subjected to accelerated weathering by heating them at 383° K in an air oven for 16 hours.

(c) Transalkylation. The procedure for transalkylation was essentially the same as that used by Heredy and Neuworth. Briefly, coal (10 g) was slurried with phenol (100 g, Aldrich) in a three-necked round-bottomed flask equipped with a condenser and a thermometer, and heated to 373° K using a water bath. Boron trifluoride (Matheson) was bubbled through the coal-phenol slurry for 6 hours. The effluent gases were passed through saturated solution of sodium carbonate to neutralize the acids. At the end of 6 hours, BF₃ flow was stopped and the flask was purged with N₂ to remove any unreacted BF₃ and gaseous HF produced by the hydrolysis of BF₃. The reaction mixture, which now was a viscous suspension, was poured into 1 litre of ice-cold water. Sodium carbonate was added to the aqueous slurry with vigorous stirring until the aqueous layer was neutral. The neutralized reaction mixture was extracted successively with ether and toluene. Preliminary analyses by GC and HPLC indicated that the ether extract contained predominantly phenol and small quantities of coal-derived products. The toluene extract also contained phenol, but had a much larger proportion of coal-derived materials than the ether extract.

(d) Analyses of the Reaction Products. The ether and toluene extracts from the transalkylation reactions of fresh and weathered coals were analyzed by GC/MS on a VG-7070HS mass spectrometer in the EI mode. The mass spectrometer was interfaced with a Hewlett-Packard 5790 gas chromatograph. The GC column was a 35 meter long capillary with DB-1 as the stationary phase. A temperature program of 423-623° K at 5°/minute was used during the analysis. It was suspected that some of the high molecular weight phenolic compounds produced during the reaction may not be volatile enough for GC analysis. Therefore, the reaction mixture was silylated using N,O-bis trimethylsilyl trifluoroacetamide (BSTFA) prior to analysis. Silylation of phenols converts them to silyl ethers, whose boiling points are considerably lower than those of the phenols. This procedure thus makes high molecular weight phenols more amenable to GC analysis. Bis-2 and bis-4 hydroxyphenyl methane were used as internal standards for quantification.

RESULTS AND DISCUSSION

Transalkylation involves the transfer of alkyl groups between aromatic nuclei, usually in the presence of strong Lewis acids. Heredy and Neuworth used this reaction to "depolymerize" coal. As a result of the reaction of coal with BF₃ and phenol, the solubility of coal in phenol or pyridine increased substantially. Various modifications of this reaction have since been reported. Transalkylation reactions in the presence of trifluoromethane sulfonic acid and aromatic hydrocarbons have recently been used by Benjamin et al. and Farcas and to identify structural features in coals and heavy petroleum ends, respectively.

It is believed that during transalkylation the aliphatic side chains and crosslinks transfer from coal, without rearrangement, to the aromatic substrate such as phenol or toluene. A typical reaction is depicted in Scheme I.
For the above reaction to occur, the aromatic nuclei in compound 1 should carry activating groups, such as hydroxyl, alkoxy, or fused ring aromatics. As a result of reaction with BF$_3$ and phenol, the macromolecular structure of coal should undergo rupture at the aliphatic crosslinks, and these crosslinks are transferred to phenol molecules to produce bisphenols. Analysis of the bisphenols should provide information on the aliphatic crosslinks present in coal structure.

In model compounds, the aliphatic side chains on aromatic nuclei transalkylate without rearrangement. However, the reaction of aliphatic crosslinks is more complicated. For example, transalkylation of 1-(4-methoxyphenyl)-3-(2-naphthyl) propane (Compound 4) under BF$_3$-phenol reaction conditions does not produce the expected 1,3-bishydroxyphenyl propane (Compound 5). Instead, it gives a variety of products resulting from the rearrangement and fragmentation of the trimethylene crosslink in Compound 4, as shown in Scheme II.

Because of the above considerations, it is not possible to determine the exact nature and concentration of the crosslinks as they are present in coals by analysis of the transalkylation products. However, a comparison of the relative concentrations of the various crosslinks in different coal samples and how they change during weathering is possible. Specifically, our aim is to compare the relative concentrations of methylene and polymethylene crosslinks in fresh and weathered coals, so that the effect of weathering on these crosslinks can be assessed.
Numerous bisphenols of the general structure 11 were detected in both the ether and toluene extracts of the transalkylation products from the fresh and weathered coal samples.

\[ \text{HOOC} \rightarrow X \rightarrow \text{OH} \]

X = straight or branched chain aliphatic crosslink

Table 2 contains a list of the aliphatic crosslinks detected in the toluene extract. Compounds with methylene crosslinks were predominant in the products from the fresh coal. This is consistent with the results of Benjamin et al.\(^\text{27}\). It is interesting to note that several branched chain crosslinks appear in the transalkylation products from both the fresh and the weathered coals. Such crosslinks in coal structure have been reported only recently. Alkyl substituted methylene and ethylene crosslinks have been detected in a Wyodak coal by Benjamin et al.\(^\text{26}\). In the present study, some of the branched chain crosslinks may have been formed by rearrangement of the straight chain crosslinks during transalkylation\(^\text{27}\).

The relative concentrations of several types of hydrocarbon crosslinks, namely methylene(-CH\(_2\)-), ethylene(-CH\(_2\)-CH\(_2\)-), methyl methylene(-CH(CH\(_3\))-), methyl ethylene(-CH(CH\(_3\))-CH\(_2\)-), ethyl methylene(-CH(CH\(_2\)-CH\(_3\))-), and propyl methylene(-CH(CH\(_2\)-CH\(_2\)-CH\(_3\))-) in the fresh and weathered San Juan coal are compared in Table 3. The concentrations are reported as a fraction of the toluene extract from the transalkylation reaction. As a result of weathering, concentrations of the most abundant crosslinks namely, methylene, ethylene, methyl methylene, and ethyl methylene groups are reduced by factors of 6, 14, 6, and 9 respectively. The differences in the concentrations of larger crosslinks were not measured because of their low abundance in the transalkylated products.

The results in Table 3 clearly indicate that the aliphatic crosslinks have been altered significantly by oxidative weathering. The question is: what are these crosslinks converted to? Liotta et al. have detected, by infrared analysis, increases in carboxylic acid groups and ether linkages after long term ambient temperature weathering of an Illinois #6 coal\(^\text{16}\). Painter et al. have obtained infrared spectroscopic evidence for a decrease in the aliphatic stretching intensity (2900 cm\(^{-1}\) region) and an increase in the carbonyl stretching (1700-1765 cm\(^{-1}\) region) after weathering of a highly caking Pennsylvanian coal\(^\text{27,32}\). They speculate the formation of ester groups, in addition to ketones and carboxyl groups, as a result of extended weathering at about 373° K. Jakab et al. have reported that weathering of subbituminous coals causes changes in both the aliphatic and aromatic structures of coal\(^\text{33}\). They detected, by Curie Point pyrolysis GC-MS, an increase in carbonyl groups in the coals weathered in air at 373° K. In addition, they found decreased yields of alkylaromatics and phenolics from the weathered coal compared to the fresh coal. The decrease was attributed to condensation reactions involving alkyl aromatics and phenolic
fragments resulting in large clusters. Gethner has speculated that formation of ketones, aldehydes, esters, and ethers is likely during oxidative weathering of coals at 373° K. Recently, Fuller has obtained high temperature infrared spectroscopic data which indicate that during oxidative weathering at 473° K or above, several surface groups such as ketones, aldehydes, carboxylic acids, and anhydrides of carboxylic acids are formed.

We have examined the infrared spectra of three coals before and after overnight weathering in air at 383° K. The infrared spectra of the fresh coals, their corresponding weathered samples, and the difference spectra between the weathered and fresh coals are given in Figures 1-3. Several changes due to weathering are observed. The most significant changes are the enhanced carbonyl absorptions in the 1700 cm⁻¹ region, and decreases in the aliphatic C-H absorptions in the 2850-2950 cm⁻¹ (CH stretching) and 1450 cm⁻¹ (CH₂ bending) regions. These changes are quite discernible in the difference spectra. Minor changes are observed in the aromatic CH vibrations in the 750 - 850 cm⁻¹ region as well, especially in the Elkhorn coal.

With regard to the results of our infrared study, a word of caution is appropriate. The large decreases in the concentration of the aliphatic crosslinks after weathering, as measured by transalkylation (Table 3), cannot be expected to match those indicated in the difference infrared spectra between weathered and fresh coals. This is because the spectra measure the total aliphatic content of the samples, namely aliphatic crosslinks, hydroaromatics, and aliphatic side chains. In contrast, results in Table 2 show differences in relative concentrations of the aliphatic crosslinks, which represent only a small part of the total aliphatics. Furthermore, concentrations measured by transalkylation correspond to only the soluble fractions of the reaction products; some of the more complex transalkylation products may be retained in the residue itself.

Our transalkylation studies show that the concentrations of methylene and other aliphatic crosslinks decrease during oxidative weathering. The infrared analysis shows that carbonyl groups are produced during weathering. Therefore, it is quite likely that during our weathering conditions the aliphatic crosslinks are oxidized to carbonyls and/or carboxylic acid groups.

A possible mechanism of oxidation of methylene groups to carbonyl groups involves autooxidation (oxidation by molecular oxygen) at the benzylic position. Autooxidation of arylalkanes is a facile reaction with low activation energies; for example, 6.0 kcal/mole for 1,1-diphenylethane and, 13.3 kcal/mole for toluene²⁵,³⁸. Autooxidation of coals can be initiated by abstraction of a benzylic hydrogen atom by free radicals already present in coals³⁷,³⁸. The resulting benzylic radical then reacts with oxygen to form a peroxyradical, which abstracts a H-atom from elsewhere in the coal "molecule" to form a hydroperoxide. Formation of hydroperoxide during weathering is speculated by other workers as well¹⁶,⁴⁵,⁴¹. The hydroperoxide can undergo homolysis at the peroxy bond (activation energy = 35 kcal/mole) to generate an alkoxyl radical (Scheme III) which can undergo various reactions to produce carbonyl compounds. Some of the possible reactions of the alkoxyl radical are represented in Schemes IV and V.
Scheme III. Possible Oxidation Pathways

\[
\begin{align*}
\text{Ar-CH}_2\text{-Ar} & \xrightarrow{R'} \text{Ar-CH-CH-CH}_2\text{-Ar} \\
\text{O} & \xrightarrow{-\text{RH}} \text{Ar-CH}_2\text{-Ar} \\
\text{O} & \xrightarrow{\text{O-O-H}} \text{Ar-CH}_2\text{-Ar} \\
\end{align*}
\]

Scheme IV. Possible Oxidation Pathways (contd.)

\[
\begin{align*}
\text{Ar-CH-CH}_2\text{-Ar} & \xrightarrow{\text{RH}} \text{Ar-CH-CH}_2\text{-Ar} \\
\text{O} & \xrightarrow{\text{O}} \text{Ar-CH}_2\text{-Ar} \\
\end{align*}
\]

Scheme V. Possible Oxidation Pathways (contd.)

\[
\begin{align*}
\text{Ar-CH-CH}_2\text{-Ar} & \xrightarrow{-\text{RH}} \text{Ar-CH-CH}_2\text{-Ar} \\
\text{O} & \xrightarrow{\text{Ar-C-CH}_2\text{-Ar}} \text{Ar-CH-CH}_2\text{-Ar} \\
\end{align*}
\]
There is ample evidence in the literature for conversion of reactive hydrocarbons to carbonyl compounds by autooxidation\textsuperscript{52-54}. In coals, the final products of autooxidation under the conditions used in the present study could be a mixture of carbonyl and carboxylic acid surface groups. Under mild oxidation conditions, a different set of functional groups such as ethers as proposed by Liotta et al.\textsuperscript{16} or epoxides as suggested in Scheme V could be formed. There are numerous examples of alkoxy radicals rearranging to epoxides\textsuperscript{48-51}. Choi and Stock have shown that ethers can be produced from benzhydrol structures, which are invoked as intermediates in Scheme IV\textsuperscript{52}. At higher temperatures, the epoxides and ethers are unstable and may rearrange to carbonyl compounds.

CONCLUSIONS

Oxidative weathering of coal causes a significant decrease in the concentration of aliphatic crosslinks; the relative decrease was determined by acid-catalyzed transalkylation of coal with phenol. Infrared analysis of the raw and weathered coals indicate that the hydrocarbon crosslinks are converted to carbonyl groups. Plausible explanations have been offered for the formation of carbonyl groups from aliphatic crosslinks.

ACKNOWLEDGEMENTS

The authors wish to thank J. E. Duffield, Cynthia Neu and Jean Schaap for technical assistance; R. E. Pauls and R. W. McCoy for GC and HPLC analysis; G. G. Jones for GC/MS analysis, and A. B. Hossman for helpful discussions.

REFERENCES

34. Gethers, J. S. Fuel 1985, 64, 1443.
### TABLE I. Proximate and Ultimate Analyses of Coals

<table>
<thead>
<tr>
<th></th>
<th>San Juan</th>
<th>I1l #6</th>
<th>Elkhorn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate Analysis (wt %, dry basis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>11.4</td>
<td>11.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>44.2</td>
<td>39.7</td>
<td>38.7</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>44.4</td>
<td>48.5</td>
<td>54.8</td>
</tr>
<tr>
<td>Ultimate Analysis (wt %, dmm*)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>78.9</td>
<td>78.9</td>
<td>85.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.0</td>
<td>5.4</td>
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<tr>
<td>Nitrogen</td>
<td>1.6</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.0</td>
<td>4.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Oxygen (by diff.)</td>
<td>12.4</td>
<td>10.0</td>
<td>6.3</td>
</tr>
</tbody>
</table>

*Dry, mineral matter-free basis

### TABLE II. Crosslinks Detected in the Transalkylated Products

<table>
<thead>
<tr>
<th>Crosslink</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene</td>
<td>-CH₂⁻</td>
</tr>
<tr>
<td>Ethylene</td>
<td>-CH₂-CH₂⁻</td>
</tr>
<tr>
<td>Methylmethylene</td>
<td>-CH(CH₃)-</td>
</tr>
<tr>
<td>Ethylethylene</td>
<td>-CH(CH₂CH₃)-</td>
</tr>
<tr>
<td>Propyl methylene</td>
<td>-CH(CH₂CH₃CH₃)-</td>
</tr>
<tr>
<td>Methylethylene</td>
<td>-CH(CH₃)-CH₂⁻</td>
</tr>
<tr>
<td>Ethylethylene</td>
<td>-CH(CH₂CH₃)-CH₂⁻</td>
</tr>
<tr>
<td>Butylethylene</td>
<td>-CH(CH₂CH₂CH₃CH₃)-</td>
</tr>
</tbody>
</table>
### TABLE III. Relative Concentrations of Crosslinks in the Transalkylated Products from Fresh and Weathered San Juan Coal.

<table>
<thead>
<tr>
<th>Crosslink</th>
<th>Relative Concentration</th>
<th>Ratio: Fresh/Weathered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Weathered</td>
</tr>
<tr>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>5.16</td>
<td>0.85</td>
</tr>
<tr>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>1.8</td>
<td>0.13</td>
</tr>
<tr>
<td>-CH(CH&lt;sub&gt;3&lt;/sub&gt;)-</td>
<td>1.08</td>
<td>0.17</td>
</tr>
<tr>
<td>-CH(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>1.04</td>
<td>0.11</td>
</tr>
<tr>
<td>-CH(CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;)-</td>
<td>0.67</td>
<td>0.09</td>
</tr>
</tbody>
</table>
Figure 1. Infrared spectra of San Juan coal
A. Fresh coal, B. Weathered coal, and C. Difference spectrum (B–A).
Figure 2. Infrared spectra of Illinois #6 coal
A. Fresh coal, B. Weathered coal, and C. Difference spectrum (B−A).
Figure 3. Infrared spectra of Elkhorn coal
A. Fresh coal, B. Weathered coal, and C. Difference spectrum (B–A).
NOVEL C_{22}^{24} ALKENE DIMERS FORMED VIA TITANIUM-PROMOTED REDUCTIVE DIMERIZATION OF POLYCYCLIC CAGE KETONES: POTENTIAL NEW FUELS FOR AIRBREATHING MISSILES

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INTRODUCTION

The development of new high-energy hydrocarbon fuels for use in air-breathing missiles has been the objective of a number of investigations which have received support during the past decade through programs sponsored by the Air Force Systems Command and/or the Naval Air Systems Command. The key characteristics which must be met by potential cruise missile fuels have been described by Rurdette and coworkers. A primary requirement in this regard is that candidate fuels must possess high net volumetric heat of combustion (preferably greater than 160,000 BTU/gallon). In order to meet the primary requirement of high net volumetric heat of combustion, hydrocarbon systems, C_{n}H_{m}, have been sought that maximize the ratio n/m. Bridged ring (polycyclic) hydrocarbon systems, by virtue of their high densities (concomitant with their compact structures), are particularly promising candidate fuels. Compounds of this type already have been utilized extensively as fuels for air-breathing missiles.

In the early stages of our study, one-pound samples of two particularly promising fuel candidates, 1 (heptacyclo[6.6.0.0^{2}.6.0^{3}.13.0^{4}.11.0^{5}.0^{9}.10.14]tetradecane, HCTD) and 2 (pentacyclo[5.4.0.0^{2}.6.0^{3}.10.0^{5}.9]undecane, PCUD, structures shown in Scheme 1) were synthesized. Both 1 and 2 display high densities (1.26 and 1.23 g-cm^{-3}, respectively). The performance of each compound as a ramjet fuel has been evaluated by personnel at the Naval Weapons Center. In addition, several derivatives of 1 and of 2 have been synthesized.
One difficulty attendant with the use of both HCTD and PCUD as fuels is their volatility. Although they are both high-melting solids, both hydrocarbons sublime readily and can escape from the binder (e.g., hydroxy-terminated polybutadiene, HTPB) on long standing at ambient temperature. In an effort to minimize the volatility of these systems (and thereby to improve their combustion and storage characteristics) without sacrificing other desirable fuel properties, we have undertaken the synthesis of HCTD and PCUD oligomers. We now report on the synthesis of some isomeric C_{22}H_{24} alkenes obtained via titanium-promoted reductive dimerization\(^ {12} \) of polycyclic cage C_{11}H_{20} ketones and some aspects of the chemistry of the alkene dimers thereby obtained.

**RESULTS & DISCUSSION**

C_{22}H_{24} Alkene Dimers Derived from PCUD-8-one. Our synthesis of PCUD alkene dimers, obtained via reaction of low-valent titanium with PCUD-8-one (3), is shown in Scheme 2. Four dimers potentially can result from this reaction, each of which possesses a twofold symmetry element (e.g., mirror plane, \( C_2 \) axis, or center of symmetry). In our hands, titanium-promoted reductive dimerization of 3 afforded a mixture of dimers, 4a-4d, as expected. Careful fractional recrystallization of this mixture from hexane afforded a single isomer, 4a, mp 214-215 °C, whose structure was determined via single crystal X-ray structural analysis.\(^ {13} \) Particularly noteworthy is the unusually high crystal density of 4a, i.e., 1.284 g·cm\(^{-3} \) (calculated from the X-ray data).\(^ {13} \)
Subsequently, the remaining three isomers (i.e., 4b-4d) were isolated by a combination of column chromatographic techniques and fractional recrystallization. Ultimately, we hope to obtain X-ray data that will permit unequivocal characterization of each of the three remaining PCUD dimers.

Recently, a study was undertaken of electrophilic additions to these PCUD dimers (individually and in the gross mixture of four dimers that results via titanium-promoted dimerization of PCUD-8-one). This was done for several reasons: First, it was of interest to determine whether structural differences among the various dimers would lead to differences in reactivity toward the electrophilic reagent, HX. If this is indeed the case, then it may be possible to separate one or possibly two of the dimers from the mixture by taking advantage of these differential reactivities. Secondly, we anticipated that Wagner-Meerwein rearrangements might occur in carbonium ion intermediates, thereby leading to the formation of interesting new C$_{22}$ compounds that are not easily accessed via direct, titanium-promoted dimerization reactions. Finally, we are interested in determining whether or not structural differences among the various PCUD dimers might...
affect the mode of addition (syn vs. anti) of HX across the C=C double bond of each dimer.

The results of electrophilic addition of trifluoroacetic acid to a mixture of the four PCUd dimers (Scheme 2) are shown in Scheme 3. When the reaction with CF$_3$CO$_2$H was performed at room temperature in chloroform solvent, a mixture of two trifluoroacetate adducts (5a and 5b) was formed (60%) along with a mixture of two unreacted PCUd dimers (16.7%). The mixture of 5a and 5b was then subjected to hydrolysis with aqueous base, thereby affording a mixture of alcohols, 6a and 6b. The resulting mixture of alcohols was oxidized subsequently by using pyridinium chlorochromate (PCC) in methylene chloride solvent. The product was found to be a mixture of two isomeric ketones, 7a and 7b, which could be separated by flash column chromatography. The structures of 7a and 7b each have been established unequivocally by single crystal X-ray structural analysis.

Subsequently, the unreacted dimer (recovered from the above reaction; mixture of two isomers) was treated with trifluoroacetic acid in refluxing chloroform. Addition of trifluoroacetic acid to the C=C double bond in the mixture of dimers occurred under these conditions. Basic hydrolysis of the trifluoroacetate adduct followed by oxidation with PCC again afforded a mixture of 7a and 7b.

Recently, we have studied the Wolff-Kishner reduction of isomERICALLY pure ketones 7a and 7b. Of particular interest is the fact that the hydrocarbons thereby obtained differ substantially in melting point. The product of Wolff-Kishner reduction of 7a (i.e., 8a) displays mp 114-115 °C, whereas the corresponding product obtained by Wolff-Kishner reduction of 7b (i.e., 8b) displays mp 74-75 °C. The structure of 8a has been determined by X-ray crystallographic methods (Scheme 4); the calculated crystal density of 8a was found to be 1.290 g-cm$^{-3}$.15
Scheme 3

TiCl₄, 2n, pyridine, THF
H₂, reflux 3 days (44%)

4a-d (mixture of four isomers)

CF₃CO₂H, CHCl₃
room temperature 5 hours

+ unreacted PCUD dimers (two isomers, 17%)

5a + 6b (mixture of isomers, 60%)

10% eq. NaOH
THF, room temp.

PCC, CH₂Cl₂, room temp.
1.5 hours (74%)}

6a + 6b (mixture of isomers)

7a (mp 105.0-105.5 °C)
7b (mp 106.5-107.0 °C)

Structure drawing of 7a

Structure drawing of 7b
C_{22}H_{24} Alkene Dimers Derived from D₃-Trishomocubanone. As an extension of the foregoing study, alkene dimers have been synthesized via titanium-promoted reductive dimerization of the D₃-trishomocubanone (9). In this case, only two dimers [i.e., 10a (meso) and 10b (d,l)] can result from this reaction (Scheme 5). Indeed, a 1:1 mixture of 10a and 10b was obtained from this reaction. Careful fractional recrystallization of the mixture of dimers thereby obtained from ligroin afforded a single isomer, mp 246 °C. This dimer was shown to possess the meso configuration (i.e., 10a) by single crystal X-ray structural analysis. Of particular significance is the unusually high calculated crystal density of 10a, i.e., 1.302 g·cm⁻³.

More recently, the corresponding d,l dimer, 10b, mp 186 °C, has been isolated, and its structure has been determined by X-ray crystallographic methods (Scheme 5). Interestingly, the calculated crystal density of 10b (1.269 g·cm⁻³) is significantly lower than that of 10a.¹⁶

Two important results of that have emerged from the studies described above are
Scheme 5

DIMERS DERIVED FROM D_3-TRISHOMOCUBANONE

9

\[ \text{TICl}_3 \text{-Zn, THF, PYRIDINE, } H_2 \text{ REFLUX 24 H (D5)} \]

10a (MSSD)

10b (L, R)

Structure drawing of 10a

Density = 1.302 g·cm\(^{-3}\) (Calcd)

Structure drawing of 10b

Density = 1.269 g·cm\(^{-3}\) (Calcd)
noteworthy. First, the calculated crystal densities of PCUD dimer 4a, of the rearranged cage hydrocarbon 8a, and of 10a and 10b (i.e., $1.284$, $1.290$, $1.302$, and $1.269 \text{ g-cm}^{-3}$, respectively) rank among the highest known hydrocarbon densities; [compare these values with the densities of cubane ($1.29 \text{ g-cm}^{-3}$),\textsuperscript{17} 1,16-dimethyldecahedrane ($1.412 \text{ g-cm}^{-3}$),\textsuperscript{18} and dodecahedrane ($1.448 \text{ g-cm}^{-3}$)].\textsuperscript{19}

Second, it is important to note that all of the three dimeric alkenes, i.e., 4a, 10a, and 10b, whose X-ray crystal structures have been determined thus far in our study, are all $C_{22}H_{24}$ isomers that possess distinctly different crystal densities. Any of the existing calculational methods that are used to estimate crystal densities are based upon molecular formula and functional group additivity and therefore are incapable of predicting variations in densities among geometric isomers.\textsuperscript{20} Hence, contrary to the X-ray crystallographic results cited above, all of our $C_{22}H_{24}$ isomers are predicted by any of these methods to possess the same density.

**SUMMARY & CONCLUSIONS**

Our efforts to synthesize oligomers of strained polycyclic cage monomers have resulted in the synthesis of novel cage alkene dimers 4a-4d, 10a and 10b, along with derivatives of these systems. These dimers possess unusually high crystal densities and are relatively nonvolatile; both properties are considered to be desirable for new candidate fuel systems. The electrophilic addition of trifluoroacetic acid to a mixture of PCUD alkene dimers, 4a-4d, has been studied, and several reaction products have been characterized by single crystal X-ray structural analysis. Future studies will be directed toward: (i) the synthesis of oligomers of HCTD (1) and (ii) studies of reactions of 10a and 10b with a variety of electrophiles.

**ACKNOWLEDGMENTS**

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REFERENCES AND FOOTNOTES


MODELING OF THE THERMAL STABILITY OF AVIATION FUELS

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INTRODUCTION

The detailed chemical reactions that result in fuel deposits are very complex and very poorly understood at the present. However, it has been reported by several researchers (1-6) that the reaction usually initiates with a liquid phase oxidation of the fuel, which is promoted by dissolved oxygen. Common impurities such as compounds of sulfur, nitrogen, and dissolved metals play a role by either accelerating the reactions or affecting the solubility of the degradation products. Above 750 K, the deposition reaction is characterized by the pyrolysis of hydrocarbon molecules and the scission of hydrogen.

Mayo and Lan (2) have studied the rates of oxidation and gum formation for different fuels. They used t-BuO₂ as the initiator and found that some fuels oxidized faster at 100°C than in their previous work (7) at 130°C without initiator. They proposed that gum formation starts with coupling of two alkyl peroxy radicals in the chain termination of oxidation and that growth beyond dimer depends on converting dimer to peroxy radicals by chain propagation.

The general free radical mechanism agreed upon by several researchers and outlined by Foder et al. (5) is given below.

\[
\begin{align*}
\text{Formation of alkyl peroxide: } & \text{RH} + \text{O}_2 \rightarrow \text{ROOH} \\
\text{Initiation: } & \text{ROOH} \rightarrow \text{HO}^\cdot + \text{RO}^\cdot \\
\text{Propagation: } & \text{HO}^\cdot + \text{RH} \rightarrow \text{R}^\cdot + \text{H}_2\text{O} \\
& \text{RO}^\cdot + \text{RH} \rightarrow \text{R}^\cdot + \text{ROH} \\
& \text{R}^\cdot + \text{O}_2 \rightarrow \text{RO}_2^\cdot \\
\text{Termination: } & \text{RO}_2^\cdot + \text{RO}_2^\cdot \rightarrow \text{Products} \\
& \text{R}^\cdot + \text{R}^\cdot \rightarrow \text{R} - \text{R}
\end{align*}
\]

A study was done at Advanced Fuel Research, Inc. (AFR) in which Fourier Transform Infrared Spectroscopy (FT-IR) and Field Ionization Mass Spectrometry (FIMS) were used to study the products from fuel degradation (soluble gums, insoluble gums, and deposits removed on a wire collection probe) (8). The results indicated that the wire deposits were primarily long chain aliphatics (heavier than the starting fuel), which may be formed by termination steps in the above mechanism. The soluble gums were primarily lower molecular weight aliphatics and aromatics which are likely formed by the main decomposition steps. The insoluble gums were intermediate in character, although more closely resembled the wire deposits.
A detailed thermal stability model will require study of additional fuels over a wide range of conditions. A preliminary global model was developed to describe the processes influencing deposition by extending work done at the United Technologies Research Center (UTRC) (4). The UTRC model employed two steps to describe decomposition, step 1 in which fuel plus oxygen is converted into a precursor for deposit formation and step 2 in which the precursor is converted to deposit. We have added a third step for the decomposition of the precursor back to fuel and CO$_2$. In addition, we have added a mass transport step which can limit the transport of the precursor to the wall surfaces.

MODEL DEVELOPMENT

Because of the difficulty in applying the detailed deposition mechanism cited in Eqs. (1-a) through (1-h) to a multi-component fuel, global reaction mechanisms are often postulated. A global model is also more appropriate for input into a comprehensive code which also includes fluid mechanics and heat transfer.

A two-step kinetic reaction mechanism has been postulated by Giovanetti and Szetela (4) and has been successfully applied to a number of time-temperature histories of the jet fuels. There are two major drawbacks of the model: 1) It does not consider any mass transfer effects; 2) It does not have possible precursor decomposition reactions which will be relevant at high temperatures.

Marteney and Spadaccini (9) have reported deposition rates for a wide temperature range and have found that at temperatures above 645 K, there is a sudden decrease in the deposition rate. A similar trend has been found by Taylor (10). This sudden drop could be due to possible mass transport resistances at high temperatures and/or precursor decomposition. Marteney and Spadaccini (9) also studied the effect of fuel flow rate on the deposition rate. They found that the peak deposition rate occurred at a lower temperature in laminar flow, suggesting that the reaction became mixing limited at elevated temperatures.

Clark and Thomas (11) found evidence that a fuel's behavior in the JFTOT may be dominated by physical transport or chemical reaction processes and that the relative importance of these two factors is fuel dependent. They found that the weight of the carbon deposited per unit flow rate went through a maximum as the flow rate was increased from 1 ml/min to 11 ml/min. They have explained their results by 3 possible rate limiting steps and postulated that the time constant of each step is fuel and flow rate dependent.

The following summary can be made of the observations on field deposition from the experimental data reported in literature.

1. The deposition rate goes through a maximum with temperature.
2. The deposition rate goes through a maximum with length of the tube.
3. The deposition rate at low temperatures declines with prestressing.
4. The deposition rate at high temperatures does not change with prestressing.
5. The pressure does not appear to exert any influence on the deposition rate.
6. The deposition rate changes with flow rate and time of the experiment. Based on these observations the following global fuel oxidation and deposition model is proposed.
where $\text{LGFF}$ is given by the following equation

$$\frac{1}{\text{LGFF}} = \frac{1}{b} \left( \frac{1}{\text{fuel}} \right) + \frac{d}{4} \left( \frac{K_2}{\text{fuel}} \right)$$

Fuel + $\text{O}_2 \rightarrow \text{Precursor} + \text{Fuel}$  \hspace{1cm} (2-a)

Precursor + Fuel $\rightarrow \text{Deposit} + \text{Fuel}$ \hspace{1cm} (2-b)

Precursor + Fuel $\rightarrow \text{Fuel} + \text{CO}_2$ \hspace{1cm} (2-c)

It is assumed that reactions 2-a and 2-b occur in the bulk and reaction 2-c occurs on the inner wall surface. For laminar flow, a stagnant layer exists in the vicinity of the wall and the mass transfer resistance may be significant for the precursor.

The time rates of change of the active species are given by

$$\frac{d[\text{O}_2]}{dt} = -K_1 [\text{fuel}] [\text{O}_2]$$ \hspace{1cm} (3-a)

$$\frac{d[\text{precursor}]}{dt} = K_2 [\text{fuel}] [\text{O}_2] - K_3 [\text{precursor}] [\text{fuel}] - R_m$$ \hspace{1cm} (3-b)

$$\frac{d[\text{deposit}]}{dt} = 4 [\text{fuel}] [\text{precursor}]$$ \hspace{1cm} (3-c)

where the brackets $[\cdot]$ denote concentration in moles/cc and the subscript $s$ denotes the concentration at the inner surface of the tube. The mass transfer rate, $R_m$, is given by

$$R_m = K_m \cdot S \cdot ([\text{precursor}] - [\text{precursor}]_{s})$$ \hspace{1cm} (4-a)

where $K_m$ is the mass transfer coefficient (cm/sec) and $S$ is surface area per unit volume (cm$^{-1}$)

$$S = \frac{4}{d}$$ \hspace{1cm} (4-b)

where $d$ is the inner diameter of the tube.

If we equate the mass transfer rate to the deposition rate (assuming steady state), we get

$$R_m = K_{\text{eff}} \cdot [\text{precursor}]$$ \hspace{1cm} (4-c)

where $K_{\text{eff}}$ is given by the following equation

$$\frac{1}{K_{\text{eff}}} = \frac{1}{K_2 / [\text{fuel}]} + \frac{d}{4} / K_m$$ \hspace{1cm} (4-d)

The mass transfer coefficient, $K_m$, is estimated by using heat transfer analogy.

The Nusselt number for heat transfer for laminar flow is given by the Seider-Tate equation (12). The Nusselt number for mass transfer can be written as

$$\text{Nu}_{\text{AB}} = 1.86 \cdot \text{Re}^{1/3} \cdot \text{Sc}^{1/3} \cdot \left( \frac{d}{L} \right)^{1/2}$$ \hspace{1cm} (5-a)

where Re and Sc are the Reynolds and Schmidt numbers, respectively, and $L$ is the length of the tube.
Martelney and Spadaccini (9) have given the heat transfer characteristics of JP-5 and found that for the transition and turbulent region, a simple Dittus-Boelter equation could be used to describe the heat transfer characteristics.

Thus for the non-laminar region, the Nusselt number for mass transfer can be written as

\[ \text{Nu}_{AB} = 0.023 \; \text{Re}^{0.8} \; \text{Pr}^{0.4} \]  

(5-b)

The mass transfer coefficient, \( K_m \), is then given by the following equation

\[ K_m = \text{Nu}_{AB} \cdot \frac{D^*_{AB}}{d} \]  

(5-c)

where \( D^*_{AB} \) is the binary diffusivity of the precursor-fuel system.

The binary diffusivity can be estimated by Wilke and Chang (13,14) as follows

\[ D^*_{AB} = \frac{(117 \cdot 3 \times 10^{-13}) \; (Q \; M)^{0.8} T}{\mu \nu_A} \]  

(6)

where \( D^*_{AB} \) = diffusivity of A in very dilute solution in Solvent B, \( m^2/s \), \( M_B \) = molecular weight of solvent, kg/kmol, \( T \) = temperature, K, \( \mu \) = solution viscosity, kg/m \cdot s, \( \nu_A \) = solute molar volume at normal boiling point, \( m^3/kmol \), \( Q \) = association factor for solvent and is 1.0 for unassociated solvents. \( \nu_A \) can be estimated from the molecular formula of the diffusing species and the values of atomic and molecular volumes (15).

**MODEL PREDICTIONS**

The experimental data used in the modeling has been taken from the NASA report by Giovanetti and Szetela (4). As discussed above, they had proposed a two-step reaction model. Their model curves are compared with the experimental data for three cases in Figs. 1a, 2a, 3a, respectively. The experimental data of Fig. 2a was used to calibrate the model and hence the fit to it is the best of the three cases. There was a discrepancy in the UTRC model. In order to fit the data, the initial oxygen concentration in fuel was assumed to be 16% of the saturation value. In addition, the mass transfer effects and precursor decompositions, which yield lower deposit formation rates at high temperatures were also neglected.

The results of the simulation of the model which included mass transfer effects are shown in Figs. 1b, 2b, and 3b. It can be seen that the model underpredicts the deposit formation at high temperatures where mass transfer effects are likely to be important. At low temperature, the model predictions are slightly improved. Thus even at the low temperature, some mass transfer resistance is present due to the very low velocity used in this experiment.

When the model constants were fitted in the UTRC work, the mass transfer effects were neglected and hence the frequency factor and activation energy for the deposit formation reaction were the global rate instead of the true kinetic rate. Consequently, in order to fit the data with mass transfer, the frequency factor or activation energy had to be changed. In addition, the initial oxygen concentration was made equal to the saturation value. The frequency factor of the reaction for deposit formation was kept constant and the activation energy was increased from 31,000 kcal/mole to 32,600 kcal/mole. The results of these simulations are given in Figs. 1c, 2c, and 3c, respectively. By this change, the experimental data at low temperature (low velocity) and high temperature (high velocity) were predicted...
very well but the data at high temperature (low velocity) showed a leveling effect after distance of 60 cm and the model predicted an increasing trend of deposit formation even at distance of 120 cm.

The above observation suggested that the leveling off of the deposit formation is due to the precursor decomposition. This would also explain the trend of lower deposit formation at higher temperatures. A third reaction of precursor decomposition was incorporated in the model with the activation energy of 32,600 and frequency factor of $2.0 \times 10^{14}$. The results of these simulations are given in Fig. 1d, 2d, and 3d, respectively. The model now seems to predict the data very well for all the three cases.

Giovanetti and Szetela (4) have also measured the deposit formation for the fuel Suntech A. The major differences between fuel Jet A and the fuel Suntech A are in the organic oxygen content, the aromatic and paraffins content and in the amount of trace elements. Based on the speculations of the various researchers reported in literature, Suntech A would be more reactive fuel that Jet A and consequently deposit formation will be higher than Jet A under identical stressing conditions. This kind of behavior was found by Giovanetti and Szetela (4) and it was reported that the carbon deposition rates for Suntech A were as high as a factor of ten greater than those for Jet A.

The UTRC model and the AFR model were exercised over two time-temperature histories for Suntech A. The deposit formation was underpredicted, which is attributed to the higher reactivity of Suntech A than Jet A. The fuel reactivity would influence the rate of the precursor formation and possibly of deposit formation. Hence the rates of these reactions were increased 40 times by increasing the frequency factor. The results of these simulations are shown in Figs. 4a and 4b. The low temperature deposit formation is predicted very well but the high temperature data are underpredicted.

Since Suntech A had a higher organic oxygen content than Jet A and the chemical composition was different (i.e. more aromatic than Jet A), the oxygen solubility and/or initial precursor concentration could be different. In our model, the initial precursor concentration is assumed to be zero. Hence the initial oxygen concentration was doubled and the rates of precursor and deposit formation were increased 20 times in the Jet A parameters. The results of these simulations are shown in Figs. 4c and 4d. The low temperature data is predicted equally well but the predictions at high temperatures are greatly improved. This result suggests that the knowledge of precursor concentration in the fuel may be important and the deposit formation may be greatly enhanced if the oxygen solubility in the fuel is higher and/or the fuel contains oxygenated species to begin with.

Sensitivity Analysis - The AFR model is a three reaction model which also includes mass transfer effects. A preliminary sensitivity analysis for the reaction parameters was done by varying the frequency factor so that the rate constants were increased by an order of magnitude on either side of the base case. The mass transfer effects were studied by varying the diffusivity.

(a) Variations in Diffusivity - This was achieved by varying the constant in the Stokes-Einstein (16) equation ($D_{\text{eff}} = \text{Constant}$). The base case used for the sensitivity analysis was that of fuel Jet A under high temperature and low velocity conditions where the mass transfer effects will have the maximum impact on deposit formation. Since the binary diffusivity of the precursor in the fuel is estimated by correlation, the sensitivity of this estimation was done and is shown in Fig. 5a. The effect of increasing the diffusivity significantly increases the amount of deposit formation and this clearly shows the base case chosen is mass transfer limited as expected.
(b) Variations in A(1) - The rate constant, $K_1$, of the reaction forming precursor was varied by varying the frequency factor. The results are shown in Fig. 5b. It is interesting to note that lowering the rate constant by an order of magnitude results in significantly lowering the amount of deposit formation but increasing by an order of magnitude does not change the amount of deposit formation very much. This suggests that the precursor formation rate is not always limiting the deposition process.

(c) Variations in A(2) - The rate constant, $K_2$, of the reaction forming deposit was varied by varying the frequency factor. The results are shown in Fig. 5c. An effect similar to that observed for the variation of $K_1$ is seen for variation of $K_2$. Even though $K_2$ was increased by an order of magnitude, the amount of deposit formation did not increase very much. This reinforces the fact that the base case is mass transfer limited. Lowering of $K_2$, however, did decrease the amount of deposit formation.

(d) Variations in A(3) - The rate constant, $K_3$, of the reaction involving precursor decomposition was varied by varying the frequency factor. The results are shown in Fig. 5d. Since increasing this rate reduces the precursor concentration, the deposit formation is reduced. Lowering the rate by an order of magnitude does not increase the deposit formation by a large amount but increasing the rate did decrease the deposit formation.

Predictions of AFR Data - The results shown in Fig. 6 show that the model can predict the maximum in deposit measured in our experiments (8,17). This maximum cannot be predicted by the UTRC model.

SUMMARY

A preliminary global model was developed extending the work done at UTRC. This new model which includes mass transfer and a precursor decomposition step can predict variations in deposit formation with fuel type, flow rate, residence time, and temperature-time history. This initial modeling effort has indicated that the measurement of the deposit precursors in addition to the deposit formation is clearly needed for model discrimination purposes. The use of on-line FT-IR diagnostics used in a related study (8,17) will help to identify the different precursors and their concentration behavior with temperature and residence time.

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Figure 1. Predicted and Measured Deposit Species Concentration - Tube Position Histories for Jet A Flowing in a Heated Tube - Low Temperature and Low Velocity Condition. a) UTRC Model \( (O_2) \) init = \( 2.25 \times 10^{-7} \) moles/cc, \( E(2) = 31,000 \) cal/gmole, \( E(3) = 0 \) cal/gmole, b) AFR Model \( (O_2) \) init = \( 2.25 \times 10^{-7} \) moles/cc, \( E(2) = 31,000 \) cal/gmole, \( E(3) = 0 \) cal/gmole, c) AFR Model \( (O_2) \) init = \( 1.40 \times 10^{-6} \) moles/cc, \( E(2) = 32,600 \) cal/gmole, \( E(3) = 0 \) cal/gmole, and d) AFR Model \( (O_2) \) init = \( 1.40 \times 10^{-6} \) moles/cc, \( E(2) = 32,600 \) cal/gmole, \( E(3) = 32,600 \) cal/gmole. Data from Ref. 4.

Figure 2. Predicted and Measured Deposit Species Concentration - Tube Position Histories for Jet A Flowing in a Heated Tube - High Temperature and Low Velocity Condition. a) UTRC Model \( (O_2) \) init = \( 2.25 \times 10^{-7} \) moles/cc, \( E(2) = 31,000 \) cal/gmole, \( E(3) = 0 \) cal/gmole, b) AFR Model \( (O_2) \) init = \( 2.25 \times 10^{-7} \) moles/cc, \( E(2) = 31,000 \) cal/gmole, \( E(3) = 0 \) cal/gmole, c) AFR Model \( (O_2) \) init = \( 1.40 \times 10^{-6} \) moles/cc, \( E(2) = 32,600 \) cal/gmole, \( E(3) = 0 \) cal/gmole, and d) AFR Model \( (O_2) \) init = \( 1.40 \times 10^{-6} \) moles/cc, \( E(2) = 32,600 \) cal/gmole, \( E(3) = 32,600 \) cal/gmole. Data from Ref. 4.
Figure 3. Predicted and Measured Deposit Species Concentration - Tube Position Histories for Jet A Flowing in a Heated Tube - High Temperature and High Velocity Condition. a) UTRC Model \( (\text{O}_2) \) \( \text{init} = 2.25E-7 \text{ moles/cc} \), \( E(2) = 31,000 \text{ cals/gmole} \), \( E(3) = 0 \text{ cals/gmole} \), b) AFR Model \( (\text{O}_2) \) \( \text{init} = 2.25E-7 \text{ moles/cc} \), \( E(2) = 31,000 \text{ cals/gmole} \), \( E(3) = 0 \text{ cals/gmole} \), c) AFR Model \( (\text{O}_2) \) \( \text{init} = 1.40E-6 \text{ moles/cc} \), \( E(2) = 32,600 \text{ cals/gmole} \), \( E(3) = 0 \text{ cals/gmole} \), and d) AFR Model \( (\text{O}_2) \) \( \text{init} = 1.40E-6 \text{ moles/cc} \), \( E(2) = 32,600 \text{ cals/gmole} \), \( E(3) = 32,600 \text{ cals/gmole} \). Data from Ref. 4.

Figure 4. Predicted and Measured Deposit Species Concentration - Tube Position Histories for Suntech A Flowing in a Heated Tube - Low Velocity Condition. \( E(1) = 17,000 \text{ cals/gmole} \), \( E(2) = 32,600 \text{ cals/gmole} \), \( E(3) = 32,600 \text{ cals/gmole} \) and \( A(3) = 0.2E15 \). a and c are Low Temperature and b and d are High Temperature Conditions. a and b) \( (\text{O}_2) \) \( \text{init} = 1.40E-6 \text{ moles/cc} \), \( A(1) = 0.14E12 \), \( A(2) = 0.8E16 \) and c and d) \( (\text{O}_2) \) \( \text{init} = 2.80E-6 \text{ moles/cc} \), \( A(1) = 0.07E12 \), \( A(2) = 0.4E16 \). Data from Ref. 4.
Figure 5. Effect on Deposit Formation of: a) Diffusivity, $D_{AB}$, b) Rate Constant, $k_1$, c) Rate Constant, $k_2$, and d) Rate Constant, $k_3$ for Fuel Jet A under High Temperature and Low Velocity Conditions. Base Case: $D_{AB}/T = 0.334E-9$, $A(1) = 0.35E10$, $A(2) = 0.2E15$, $A(3) = 0.2E15$. Data from Ref. 4.

Figure 6. Comparison of AFR Model Predictions with Deposition Rate for Aerated JP-5.
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A Review of Computational Approaches for Chemically Reacting Flows

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INTRODUCTION

Three-dimensional combustor calculations involve detailed modeling of several important physical processes. Airflow, chemical reactions, fuel sprays, and turbulence are just a few of the physical processes that must be described. Many of these processes occur on both a molecular and a macroscopic scale. To exactly describe these processes numerically, one must resolve these scales on a computational mesh. This is clearly beyond current computational resources. To make the computational task tractable, we introduce modeling assumptions. These modeling assumptions limit the generality of the computational flow code, but it is hoped that the dominant physics remain correctly represented.

Modeling assumptions are only the first limit of generality introduced when developing a combustor flow code. A further limit is introduced by the need to approximate the modeled equations before they are solved numerically. This approximation process can significantly affect the accuracy of a model prediction.

In view of all these factors, a combustor designer cannot be expected to fully embrace a computer model prediction. If a clear distinction between modeling errors and numerical approximation errors cannot be made, then the designer is left with a very unreliable computational tool.

The tremendous growth in computing power, however, has significantly improved our ability to address these issues. Faster computational speeds and larger memories has permitted the development of more complex turbulence/reaction models and the use of finer computational meshes. As a consequence, a new generation of computational tools are becoming available for the design of both high and low speed combustors. This review will examine some recent improvements in combustion models while noting some of the remaining roadblocks.

Discussion

This review will initially focus on the issues being examined in low speed combustion systems, and then will review some of the work being done for high speed applications. This review is not all inclusive but should be representative of the current state-of-the-art used in combustion system design.
Subsonic Combustion

The lack of shock waves and the frequently imposed assumption that acoustic waves can be neglected, significantly reduces the computational burden for subsonic reacting flows. Before examining reaction models, it is instructive to examine how well a few typical flow fields can be numerically predicted.

A number of alternatives exist to solve the fluid flow equations. The main distinguishing characteristic is how turbulence is represented. The most common approach and the least computationally taxing is to either time or Favre average the Navier Stokes equations. Closure for this class of flow codes employs some type of multi-equation turbulence model, the most common being a two-equation model, ref. 1. Figure 1 displays the results of a three-dimensional flow calculation compared to experimental data. The calculations were made using a two-equation turbulence model for two different geometries. Although the flows are highly similar, the numerical results are significantly different. To examine the effect of mesh refinement, the geometry with the least favorable agreement was used in an extensive mesh refinement study. Figure 2 displays the results of a series of progressively finer meshes. Figure 2a indicates that the mean flow field variables show significant improvement with mesh refinement. The same is true for fluctuating flow quantities as seen in figure 2b. While the trend with mesh refinement is encouraging, it is important to keep in mind the fact that this calculation was for a single, three-dimensional jet-in-crossflow, while a complete combustion system contains many jets and other complex flow features. It is impractical to consider using as many as 2 million mesh points for every complex feature of a typical combustor.

Even if one has sufficient mesh resolution, a two-equation turbulence model is inappropriate for many flows. Figure 3 displays a comparison between a calculated turbulence kinetic energy and experimental data for a two-dimensional, bluff-body, flow field, ref. 2. There is a large region in the flow field where there is a significant discrepancy between experiment and calculation. Mesh refinement does not significantly improve the comparison. The disagreement has been conjectured to be due to large scale vortical structures in the flow field. This bluff body type of flow field is sensitive to instabilities that produce vortical structures that can alter the development of the flow.

Whether or not these structures are defined as turbulence, it is clear that for some flows it is important to include these structures in the calculation. There are two computational alternatives to include these structures. The first, and most practical, is a Large Eddy Simulation (LES). Large Eddy Simulations involve the solution of the time-accurate, Navier Stokes equations to directly resolve the large scale structures and some form of a turbulence model is used to represent more "universal" small scale structures. But even for this class of computations, the lim-
itation remains the turbulence closure used to represent the so-called “universal” small scales. Figure 4 displays the results of a Large Eddy Simulation where both the vortical structure resolved in the calculation and the energy imparted by the turbulence model is shown, ref. 3. The large scale vortices resolved in the calculation agree fairly well with experimental data, but the energy in the turbulence model forms in the incorrect locations. Experimental evidence indicates that the turbulence model should form maximums in the braid region of the vortical structure, but the calculations indicate maximums in the core of the vortices. A second, and less practical approach, to resolve large scale structures is Direct Numerical Simulation (DNS). Direct Numerical Simulations resolve all scales of turbulence on a computational mesh and as a consequence this technique is only applicable for low Reynolds number flows. DNS will not be used to calculate real combustor flow fields, but it may be used to develop more appropriate turbulence models. For example, figure 5 displays the results of a Direct Numerical Simulation where several types of perturbations were added to a flow field to augment the amount of product formed, ref. 4. A dashed type in the figure indicates what would happen if just natural noise was used in the flow. Apparently, the amount of product that is formed can be increased by several factors if the proper forms of forcing are used. In an analogous manner Direct Numerical Simulations can be used to test reaction closures, ref. 5.

Supersonic Combustion

Supersonic combustion certainly imposes severe demands on computational analysis. Although the effect of turbulence may be reduced, ref. 6., it does not go away. Shock waves and the need for detailed finite rate chemistry add large demands for additional mesh resolution and long running times.

A flow field that is analogous to the one examined for subsonic flows is the supersonic jet in cross flow. Figure 6 displays the results of a calculation compared with experimental data from ref. 7. The predictions are for a scalar tracing the jet penetration. The contour level that penetrates the furthest should be compared to the data points. The comparison is very good, but it should be noted that these results are sensitive to mesh refinement. Other flow fields where the blowing rate of the jet is changed are not as well predicted.

With the combined requirement to treat finite rate chemistry and turbulence in compressible flows, Probability Density Function (PDF) methods are being developed for high speed flow codes. Some preliminary calculations, using this technique, have shown very promising results for some simple flows. It remains to be seen if an approach that is this computationally difficult can be usefully included into a design process.
Concluding Remarks

The computational approaches that can be used to calculate both subsonic and supersonic reacting flows have been examined. In general, it has been shown that none of these approaches are perfect, but the technology is rapidly developing. The most promising approaches to improved computational accuracy have been illustrated.

References

Figure 1. Comparison between experiment and calculation for two parametrically different three-dimensional flow fields.

Figure 2. The effect of mesh refinement on a comparison with experimental data for a jet-in-crossflow.

Figure 3. Comparison of a laboratory experiment with numerical prediction for a two-dimensional flow field.
Figure 4. Results of a Large Eddy Simulation of a forced shear layer.

B) Turbulence kinetic energy.

Figure 5. Temporal evolution of the product formed by a perturbed shear layer.

Figure 6. A comparison between predicted and experimental jet penetration in a supersonic flow field.
NASA has always been concerned with the development of new concepts for spacecraft and hypersonic aircraft. Vehicles and propulsion systems currently under investigation[1,2] would use novel combustion systems such as the air-breathing supersonic combustion ramjet engine (SCRAMjet) and fuels such as hydrogen. These vehicles would undergo prolonged operation in the low-density air regime where thermal and chemical equilibrium may not be maintained[3], both in the boundary layer outside the vehicle and inside the combustor. It is also not possible to completely duplicate these flight conditions in ground-based test facilities such as shock tunnels or arc-jets. As a result, extensive computer simulations of the airfoil and engine performance are being used in the development and design of these vehicles. In order to properly account for the non-equilibrium effects, detailed chemical models must be incorporated into the computational fluid dynamics (CFD) equations.

One of the tasks undertaken by the Computational Chemistry Branch at NASA Ames Research Center is to provide critically needed chemical and physical data for the CFD models that are being used to simulate the performance of these hypersonic vehicles. In order to reliably predict cross sections and rate constants for the important high-temperature collisional processes we use a three-step approach[4] as outlined below.

First it is necessary to determine an accurate potential energy surface (PES) for the reaction system as described in a previous paper of this symposium by Walch et al. The PES gives a measure of the net interatomic forces between the colliding atomic and molecular species. It is usually determined, for a small set of selected atomic geometries, as discrete energies resulting from large-scale ab initio quantum chemical calculations. Often these data points are clustered around the saddle point or along the minimum energy path (MEP) connecting reactant and product geometries. The energy difference between the reactants and saddle point is generally comparable to the experimental activation energy.

Second, an interpolating function must be developed to provide values of the interaction energy at any atomic geometry required by the specific reaction dynam-
ics model being used. The determination of the interpolating function is not an easy task and depends, to a certain extent, on the amount of \textit{ab initio} data available as well as the nature of the system studied. In the present study, we have used the valence-bond derived LEPS\cite{5} and the Sorbie-Murrell (SM)\cite{6} approach to represent global PES and piecewise polynomial fits to represent regions around the saddle point or along the MEP. In the LEPS method, electronically excited diatomic fragment potential energy curves are treated as adjustable fitting functions to control the topography of the PES. Their parameters are adjusted to reproduce the saddle point geometry and height, if it is known, and/or some experimental measure of the reaction dynamics such as a product scattering angle or product internal state distribution. The LEPS method is generally satisfactory for simple atom-diatom exchange reactions occurring on purely repulsive potential energy surfaces. However, if a collinear approach between reactants is not favored, or if intermediate complex formation is possible, the PES cannot usually be represented by the LEPS method. A more promising method for general systems is the SM method, which is based on the sum of an arbitrary series of terms describing all possible 2-body to n-body interactions. The increased flexibility of treating each term separately is a powerful feature of the method.

The final step in the procedure is the calculation of reaction dynamics and kinetics. In general, the reaction dynamics is treated using classical mechanics\cite{7} which should not cause a significant error, especially for collisions well above threshold. Furthermore, in spite of the fact that systems containing hydrogen atoms may have important quantum effects, such as tunneling, we expect that the calculated rate constants should still be accurate at high temperatures. We also use statistical models such as canonical variational transition state theory (CVT)\cite{8} to calculate rate constants. The statistical models allow for the inclusion of quantization of energy levels and corrections for tunneling in an approximate manner.

The classical trajectory method has been a standard approach for the calculation of the dynamics and kinetics of gas phase collisions of small molecules for more than 30 years. The calculations consist of integrating the classical equations of motion for an isolated collision between the reactant species. The propagation of these equations in time for a set of initial coordinates and momenta is called the calculation of a single trajectory and corresponds to the motion of the colliding species over a time period of \approx 1 \text{ ps}. Through the application of appropriate random sampling techniques, the behavior of an ensemble of molecules with a collision frequency of \(10^{12}\) s\(^{-1}\) can be simulated by on the order of \(10^4\) trajectories.

Statistical models of chemical kinetics such as transition state theory have been in existence for more than 50 years. However, for the last 10 years, Truhlar and coworkers have systematized numerous models and concepts under the label of variational transition state theories (VTST)\cite{8}. In this model, the optimal transition state is chosen to be the location along the intrinsic reaction path for which the free energy is minimized. Some versions of VTST use quantized anharmonic descriptions
of the transition state energy levels and include tunneling corrections. The VTST model has been thoroughly tested for elementary gas phase reactions and shown to be in agreement with experimental data and the results of classical and quantum scattering calculations.

In this presentation we first demonstrate the computational methods and give details of the calculations using the air exchange reaction

\[ N + O_2 \rightarrow NO + O \]

as an example. Walch and Jaffe\[9\] have completed \textit{ab initio} calculations for this system of the two low-lying PES that connect the ground electronic states of reactants and products. These are the \( ^2A' \) and \( ^4A' \) surfaces with saddle points energies of 10.2 and 18.0 kcal/mol, respectively, referenced to the minimum in the \( N + O_2 \) asymptote (it was estimated that the calculated \( ^2A' \) saddle point energy is too high by \( \approx 2-3 \) kcal/mol). The MEP for both surfaces favored a 110° approach of the reactants. An additional complicating factor for the \( ^2A' \) PES is the presence of a deep potential well corresponding to the ground electronic state of the NO2 molecule.

 Fits to both \( N-O-O \) surfaces were obtained using a modification\[10\] of the LEPS approach: an additional angle dependent term was added to shift the favored angle of approach from collinear to 110°. The resulting potential energy function provided a satisfactory representation of the PES for the \( ^4A' \) surface where only a small amount of \textit{ab initio} data was available. It was not, however, satisfactory for the \( ^2A' \) PES. For that case, a more elaborate formulation based on the SM method has been developed\[11\]. As of this writing, the improved \( N-O-O \) doublet potential energy function has not yet been used for trajectory calculations.

We have computed thermal rate constants for the \( N + O_2 \) reaction based on ensembles of 5000 trajectories at each temperature. The results shown in Figure 1 are the combined rate constants for exchange and dissociation. The rate constants for reaction occurring on the \( ^2A' \) and \( ^4A' \) surfaces have been combined with the proper degeneracy factors of 1/6 and 1/3, respectively. Below 2000 K reaction on the quartet surface makes little contribution to the overall rate constant because of the higher energy barrier. However, the larger degeneracy factor causes this process to become dominant at temperatures greater than 3000 K. Dissociation does not contribute significantly at temperatures below 5000 K. As can be seen from the figure, the agreement between the calculated and measured rate constants\[12,13\] is quite good. Calculations of VTST rate constants for this reaction are in progress.

In addition, statistical calculations of the rate constants for the reactions:

\[ H + O_2 \rightarrow [HO_2] \rightarrow OH + O \]

and

\[ H_2 + O_2 \rightarrow H + H_2O_2 \]

will be presented. The former is an important chain branching step in \( H_2/O_2 \) combustion. We have computed high-pressure limiting rate constants for \( HO_2 \).
Figure 3. A comparison of the theoretical and experimental rate constants for \( N + O_2 \rightarrow NO + O \).

formation using the MEP from ab initio PES calculations[14,15] and will also report VTST calculations for the exchange reaction. These results will be discussed in terms of the discrepancies in the measured high-temperature rate constants. The latter reaction has been suggested as the initiation step in the \( H_2 + O_2 \) reaction mechanism. However, no experimental data exist for this process.

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AB INITIO POTENTIAL ENERGY SURFACES FOR CHEMICAL REACTIONS

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NASA is currently pursuing programs of interplanetary exploration and manned flight which require a detailed understanding of the physics and chemistry occurring in hypersonic flow fields. Specifically, research efforts have focused on the bow shock layers which form in front of hypersonic vehicles and on the combustion processes of the supersonic combustion ramjet (SCRAMjet) which will power a future generation hypersonic aircraft. The chemistry of the hypersonic flow problem is particularly complex because the reactant species are expected to have non-equilibrium rovibrational distributions [1] under conditions of temperature, pressure, and flow rates which make the experimental measurement of reaction rates extremely difficult. In the case of the SCRAMjet, the short residence times make finite rate chemistry critical to the design of the engine. Consequently, the calculation of reaction rates from first principles has become an important component of the NASA research program.

Ab initio calculations designed to investigate the potential energy surfaces (PESs) of a number of reactions involving hydrogen, oxygen, and nitrogen have now been completed. In particular, the following reactions will be discussed:

\[ N + O_2 \rightarrow NO + O \]  \hspace{1cm} (1)

\[ H_2 + O_2 \rightarrow H + HO_2 \]  \hspace{1cm} (2)

\[ H + O_2 \rightleftharpoons [HO_2] \rightarrow OH + O \]  \hspace{1cm} (3)

\[ H + N_2 \rightleftharpoons HN_2 \]  \hspace{1cm} (4a)

\[ H + HN_2 \rightarrow H_2 + N_2 \]  \hspace{1cm} (4b)

Reaction (1) is an important process in the high temperature chemistry of the bow shock layer created by the passage of hypersonic vehicles through atmospheres whose components include nitrogen and oxygen. Reaction (2) is an initiation step while

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reaction (3) represents a critical chain-branching step in the $\text{H}_2/O_2$ combustion process. Reaction (4) is a possible two-step mechanism (chaperon mechanism) for the termolecular recombination of H atoms in the presence of N$_2$ ($\text{H} + \text{H} + \text{N}_2 \rightarrow \text{H}_2 + \text{N}_2$).

The calculation of reaction rates from first principles relies on both \textit{ab initio} electronic structure theory and an appropriate dynamical theory. The first step requires the calculation of accurate approximations to the potential energy for a limited number of selected geometrical arrangements of the atoms involved in the reaction. One of several available dynamical techniques is then chosen to calculate the rate of reaction. The choice of technique is dictated both by the nature of the reaction under investigation and by the completeness of the calculated \textit{ab initio} PES. If the calculated data is limited to the stationary points of the PES, a local representation of the PES in the neighborhood of these stationary points is determined, allowing the use of only the most elementary statistical theories to calculate the rate of reaction. If there is sufficient information to characterize accurately the minimum energy path (MEP) of the reaction, then either reaction path Hamiltonian methods or more sophisticated statistical methods can be employed in the rate calculation. Finally, if the \textit{ab initio} data is sufficiently complete to permit the development of a global representation of the PES, then either classical trajectory or quantum scattering methods can be utilized to calculate the rate of reaction. Jaffe et al. will discuss the second stage of this computational procedure in a separate paper to be presented in these proceedings.

While the details of the \textit{ab initio} computations are reported in Ref. 2-5, a brief summary of the methodology is given here. The zero-order wave function is a complete active space self-consistent field (CASSCF) wave function. For a given choice of active orbitals, every possible configuration which can be constructed by distributing the active electrons among these active orbitals is included in the wave function. The orbitals and mixing coefficients of the configuration interaction (CI) expansion are then optimized. The orbitals themselves are expanded in a finite set of atom-centered basis functions. While a basis set constructed from a segmented contraction of primitive functions was used in the study of reaction (1), the remaining calculations discussed here utilized basis functions derived from the natural orbitals of CI calculations performed on the atoms (for H atom, these calculations were performed on the $\text{H}_2$ molecule). The CASSCF calculation is then followed by a multireference contracted CI calculation (CCCI) which allows single and double excitations from the set of reference configurations (the set of configurations which are most important in the CASSCF wave function).

Walch and Jaffe [2] have completed \textit{ab initio} calculations for the $^2A'$ and $^4A'$ PESs of reaction (1). These calculations indicated that the $^2A'$ surface has an early barrier of 10.2 kcal/mol, while the $^4A'$ surface exhibits a barrier of 18.0 kcal/mol.
(Note that none of the energies discussed in this paper include corrections for zero-point energy.) Initial global representations of these two surfaces (modified LEPS potential functions) have been constructed and used in a preliminary examination [6] of the kinetics of this reaction. Further, a more accurate functional representation of the $^2A'$ surface has been completed recently [7] and will be used in future studies supporting the development of aeroassisted orbital transfer vehicles (AOTVs).

An earlier $\textit{ab initio}$ study [8] of reaction (2) identified a saddle point geometry which resembles the $\text{H} + \text{HO}_2$ reactant configuration and a barrier of $6.3$ kcal/mol. A conventional transition state theory calculation (including a Wigner tunneling correction) which treated the barrier height as an adjustable parameter required a barrier of $\approx 2.7$ kcal/mol in order to reproduce the reaction rate measured experimentally at room temperature. The present $\textit{ab initio}$ calculations, using a larger basis set, estimate the barrier height to be $3.7$ kcal/mol.

The MEP for H atom addition to $\text{O}_2$ is very similar to that found in an earlier study [9] of the same reaction. At large $\text{H} - \text{O}_2$ separations, the H atom initially approaches the $\text{O}_2$ molecule at an $\text{HOO}$ angle of $\approx 119^\circ$. This angle gradually decreases to $\approx 104^\circ$, while $r_{oo}$ gradually increases as the HO bond forms. These calculations (at the CCl level of theory) exhibit a barrier to H atom addition of $\approx 0.4$ kcal/mol.

Two additional regions of the PES for reaction (3) which have not been studied previously were investigated in the current work. The first is the region which governs the exchange of the H atom between the two oxygen atoms. The saddle point for this process is found to be $\approx 13$ kcal/mol below the $\text{H} + \text{O}_2$ asymptote, making this region of the PES accessible during the formation of [HO$_2$] from both $\text{H} + \text{O}_2$ and $\text{OH} + \text{O}$. The second region is the $\text{OH} + \text{O}$ channel which is complicated by the competition between a long-range classical electrostatic force (a dipole-quadrupole interaction) which favors a linear $\text{OH} - \text{O}$ geometry, and the short-range chemical bonding interaction which favors a bent [HO$_2$] species.

The HN$_2$ species (reaction (4a)) is found to lie $\approx 3.0$ kcal/mol above the $\text{H} + \text{N}_2$ asymptote with a barrier of $\approx 12$ kcal/mol between $\text{HN}_2$ and $\text{H} + \text{N}_2$. This calculated potential well contains six quasibound (harmonic) vibrational energy levels. A conventional transition state theory calculation which approximated tunneling with a one-dimensional Eckart model estimates the lifetime of HN$_2$ in the lowest vibrational level to be less than $6 \times 10^{-9}$ s. This result is consistent with a recent experimental [10] estimate of less than $5 \times 10^{-7}$ s for this lifetime.

A plot of the potential energy for reaction (4b) is shown in the figure. There are four pathways, three of which lead to stable $\text{N}_2\text{H}_2$ species, and a fourth which leads to $\text{H}_2 + \text{N}_2$. It is expected that reaction (4b) will lead to stabilized $\text{H}_2$ since the excess energy of the reactants can be dissipated either as relative translational
energy or rovibrational energy in the products. Because there is no potential energy barrier to the formation of \( \text{H}_2 + \text{N}_2 \), it might be expected that the production of \( \text{H}_2 \) will occur at or near the gas kinetic collision frequency. Estimates of the formation and dissociation rates of \( \text{HN}_2 \) combined with an estimate of the rate for reaction (4b) would yield an overall termolecular rate (chaperon mechanism) for the recombination of H atoms in the presence of \( \text{N}_2 \).

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INTRODUCTION:

High Mach number flight requires that the scramjet propulsion system operate at a relatively low static inlet pressure and a high inlet temperature. These two constraints can lead to extremely high temperatures in the combustor, yielding high densities of radical species and correspondingly poor chemical combustion efficiency. As the temperature drops in the nozzle expansion, recombination of these excess radicals can produce more product species, higher heat yield, and potentially more thrust. The extent to which the chemical efficiency can be enhanced in the nozzle expansion depends directly on the rate of the radical recombination reactions.

Radical recombination reactions rely on collisions to stabilize products, and consequently the rates of these reactions are, in general, pressure dependent. The low pressures inherent in high Mach number, high altitude flight can, therefore, slow these reaction rates significantly, relative to their rates in more conventional propulsion systems. This slowing of the chemistry is further compounded because high Mach number flight also implies high internal velocities that result in very short residence times (millisecond time range) in a hypersonic engine. Consequently, the finite rates of these chemical reactions may be a limiting factor in the extraction of the available chemical energy. A comprehensive assessment of the important chemical processes and an experimental validation of the critical rate parameters is therefore required if accurate predictions of scramjet performance are to be obtained.

IDENTIFICATION OF CRITICAL REACTIONS:

A chemical kinetics computer simulation code has been employed for modeling the hydrogen/air combustion in a basic hypersonic ramjet engine design. The code
models the kinetics and thermomechanics of premixed, quasi-one dimensional, time-steady streamline segments. Details of the calculations and the reaction rate constants employed are presented elsewhere [1]. The code is far simpler than conventional CFD codes, and does not consider the effects of mixing, conduction, convection, or diffusion. Our motivation is not to accurately predict scramjet performance, but to assess the role of finite-rate chemistry in the combustion process and to identify key rate-limiting steps in the combustion process.

Using this code, comparisons were made, for a variety of engine designs and flight conditions, between calculations involving finite-rate chemistry and those in which equilibrium conditions are maintained. In particular, radical densities and the energy yield, i.e., the fraction of the maximum possible heat of combustion achieved, were examined. From these comparisons, we find that the use of finite-rate chemistry models in the combustor section has only a minimal effect on the predicted performance. In contrast, very large differences are observed in the nozzle expansion, driven by the rapid drop in pressure and temperature. The finite-rate chemistry model predicts significantly higher radical concentrations at the nozzle exit, with a corresponding decrease in energy yield.

A sensitivity analysis of the chemical reaction model was conducted to identify which reactions are the key rate-limiting steps in the heat release mechanism during the nozzle expansion. Most of the bimolecular reactions, such as

\[ \text{OH} + \text{H}_2 \leftrightarrow \text{H} + \text{H}_2\text{O} \]  

were found to be very fast under typical scramjet operating conditions and tend to reach a partial equilibrium. Consequently, the exact magnitude of the bimolecular reaction rate constants that are involved should have little impact on the overall chemistry. In contrast, four termolecular radical recombination reactions were found to be particularly rate- and, therefore, performance-limiting. These critical limiting reactions are:

\[ \text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \]  

\[ \text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M} \]  

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]
The important collision partners, collectively denoted as M in the above expressions, are H₂O, N₂, H₂, and possible H-atoms under typical hypersonic combustion conditions. The relative importance of these four reactions varies with equivalence ratio. All tend to be significant under stoichiometric conditions. As might be expected, the importance of reaction (3) decreases in fuel lean conditions, while reactions (4) and (5) decrease in fuel rich conditions.

The exact rate constants for these selected reactions that are used in the simulations can dramatically affect predicted combustion efficiency and engine performance. It is therefore of critical importance that the rate constants for these reactions be well determined if accurate predictions of scramjet performance are to be obtained.

The accuracy to which the rate constants for these processes are presently known was examined. Figure 1 summarizes the published data acquired over the past half century for reaction (2), where \( M = H_2O \). For references to the original studies from which these data were obtained, refer to the Leeds compilation [2]. The data in figure 1 fall into two groups, high temperature measurements around 2000K from flame and shock tube experiments, and room temperature data from flash photolysis experiments. The span in the rate constant data at either temperature is nearly two orders-of-magnitude. The solid line in the figure is the recommended value of Baulch et al. [2], but clearly the large spread in the data on which this recommendation is based reveals the unacceptably large uncertainties inherent in this value, as noted in the original compilation. Examination of the data for reaction (2) with other collision partners, M, as well as the data for reactions (3), (4), and (5) show similar uncertainties. The critical importance of these recombination reactions to nozzle performance, combined with the large unacceptable scatter in the literature data, indicate that these reactions are prime candidates for experimental study.

**EXPERIMENTAL MEASUREMENTS:**

The rate constants for reactions identified through the modeling simulations as critical for good scramjet performance are being experimentally determined using the laser photolysis / laser-induced fluorescence (LP/LIF) relaxation kinetics technique. In this technique, water vapor, containing various added amounts of hydrogen, oxygen, and/or nitrogen, is equilibrated at temperatures extending from room temperature to 1800K (3200R) and at total pressures in the range 7 - 30 psia. This equilibrium mixture will be perturbed essentially instantaneously using excimer laser photolysis so
Figure 1. Summary of published rate constant data for H + OH + M reaction.

as to increase the concentrations of the OH radicals and H atoms by

\[ \text{H}_2\text{O} + \text{hv}(193\text{nm}) \rightarrow \text{OH} + \text{H} \]  \hspace{1cm} (6).

The absolute densities of the photolytically introduced radicals can be determined from the laser fluence and an independently determined photodissociation cross section for water vapor. Laser-induced fluorescence is then used to monitor the subsequent time histories of the OH and/or H as they return to their equilibrium concentrations. The time required for the chemical system to return to equilibrium, i.e., the relaxation time, is measured and compared to predictions of the chemical kinetic modeling code under identical conditions. Since this technique simultaneously evaluates the entire relaxation mechanism, we can be assured that all key reactions are addressed in the experiment and that a self-consistent set of rate constants can be obtained.

Before beginning the recombination rate constant measurements, direct measure-
ments of the rate constant for the bimolecular reaction

\[ \text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O} \quad (1a) \]

were completed in the temperature range 800-1550K. The OH is removed by this reaction as the partial equilibration of the OH and H-atom densities is attained. Analysis of the fast OH removal rates as a function of added hydrogen yields the rate constant for the above reaction.

The rate constant for this reaction has been well determined in a number of previous studies by other workers and was recently reexamined by Michael and Sutherland [3]. They combined their shock tube data with those of Frank and Just and the flash photolysis data of Tully, Ravishankara, and co-workers, and derived the expression:

\[ k = 3.59 \times 10^{-16} T^{1.51} \exp\left(-1726 / T\right) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} , \]

which is applicable in the temperature range 250-2581 K. Our recent measurements bridge the gap between the shock tube data (1246-2581 K) and the flash photolysis data (250-1050 K) and are in very good agreement with these previous data sets in the overlap region. Our data points lie slightly above the fit expression recommended by Michael and Sutherland. We combined our data with the three data sets they used and the recently reported data [4] of Davidson, Chang, and Hanson, to derive a new expression for the rate constant:

\[ k = 3.56 \times 10^{-16} T^{1.52} \exp\left(-1736 / T\right) \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} . \]

The constants in this expression are nearly identical to those in the Michael and Sutherland expression. However, the rate constants calculated with this new expression are a few percent higher, averaged over the entire temperature range. Figure 2 shows an Arrhenius plot of our recently obtained data (LANL) along with some of the other data values obtained from published papers and used in determining the fit expression. The fit line shown in the figure is based on our recommended expression. These results are presently being prepared for publication.

The purpose of these measurements was to validate the kinetic measurement techniques employed in these experiments by reevaluating a well known rate constant, in preparation for our recombination rate constant measurements. Having achieved this objective, our studies have begun on the recombination reactions.

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Preliminary rate constant values for recombination reactions (2) and (3) have now been obtained at a single temperature (1223 K). However, the uncertainty of these measurements is at present unacceptably large. Relaxation rate measurements at this temperature for additional gas compositions are in progress. Variation of the gas composition allows different reactions to dominate the chemistry, and consequently this additional data should improve the precision of these rate constant determinations. Over the next few months, the temperature range of these measurements will be extended to the limits of our present high temperature cell (300 - 1800 K). The wide temperature range of these experiments (note Fig. 1) should allow accurate extrapolations of these new rate constants into temperature regimes of relevance for hypersonic combustion. The status of these measurements will be discussed in the presentation.

\[ k = 3.56 \times 10^{-16} T^{-1.52} \exp(-1736 / T) \]

**Figure 2.** Arrhenius plot of rate constant data for \( \text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O} \) reaction.
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HOMOGENEOUS CATALYSTS IN HYPERSONIC COMBUSTION

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INTRODUCTION

Density and residence time both become unfavorably small for efficient combustion of hydrogen fuel in ramjet propulsion in air at high altitude and hypersonic speed. Raising the density and increasing the transit time of the air through the engine necessitates stronger contraction of the airflow area. This enhances the kinetic and thermodynamic tendency of $\text{H}_2\text{O}$ to form completely, accompanied only by $\text{N}_2$ and any excess $\text{H}_2$ (or $\text{O}_2$). The by-products to be avoided are the energetically expensive fragment species $\text{H}$ and/or $\text{O}$ atoms and $\text{OH}$ radicals, and residual (2$\text{H}_2$ plus $\text{O}_2$). However, excessive area contraction raises air temperature and consequent combustion-product temperature by adiabatic compression. This counteracts and ultimately overwhelms the thermodynamic benefit by which higher density favors the triatomic product, $\text{H}_2\text{O}$, over its monatomic and diatomic alternatives.

For static pressures in the neighborhood of 1 atm ($\times/\pm 2.5$), static temperature must be kept or brought below ca. 2400 K for acceptable stability of $\text{H}_2\text{O}$. In contrast, temperatures exceeding ca. 3200 K at these static pressures actually give net endothermic pyrolysis of $\text{H}_2$ and $\text{O}_2$, with more atoms than $\text{H}_2\text{O}$. Some relief from these limitations on efficient use of low-density air as an oxidant may be realized by expenditure of excess, initially cold fuel whose specific heat protects stability of $\text{H}_2\text{O}$ and whose ejected mass contributes to thrust.
Another measure, whose requisite chemistry we address here, is to extract propulsive work from the combustion products early in the expansion. The objective is to lower the static temperature of the combustion stream enough for $\text{H}_2\text{O}$ to become adequately stable before the exhaust flow is massively expanded and its composition "frozen." Prospective success of this measure in an acceptable expansion length is limited by the kinetics of the three-body "recombination" mechanism by which the composition of combustion products can shift exothermically.

We proceed to address this mechanism and its kinetics, and then examine prospects for enhancing its rate by homogeneous catalysts.

**UNCATALYZED RECOMBINATION**

*Recombination Mechanism*

The most facile steps by which net recombination is understood to occur among the fragments of $\text{H}_2\text{O}$ are:

\[
\begin{align*}
\text{H} + \text{H} + \text{M} & \rightarrow \text{H}_2 + \text{M} \\
\text{H} + \text{OH} + \text{M} & \rightarrow \text{H}_2\text{O} + \text{M} \\
\text{H} + \text{O} + \text{M} & \rightarrow \text{OH} + \text{M}
\end{align*}
\]

and the sequence

\[
\begin{align*}
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M}
\end{align*}
\]

followed by

\[
\begin{align*}
\text{H} + \text{HO}_2 & \rightarrow \text{H}_2 + \text{O}_2
\end{align*}
\]

or

\[
\begin{align*}
\text{OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]
The respective exothermicities of steps (1) through (3), expressed as $-\Delta H$ in kcal/mole at zero Kelvin and rounded to the nearest whole number, are: 103, 118, and 101. The corresponding values for steps (4) through (6) are: 49, 54, and 69. The net effects of the (4),(5) and (4),(6) sequences are indistinguishable from (1) and (2), respectively. For modeling, we use a more complete mechanism that includes alternate product channels of step (5) and a step analogous to (6) in which O-atom replaces OH. To set the stage here for the role of catalysts, we proceed without these other steps.

In compositions that are more or less hydrogen-rich, steps (1) and (2) contribute in parallel, in proportions governed by the H/OH ratio and the individual rate coefficients for each step with H$_2$O, N$_2$, H$_2$, and even atomic H as third bodies, collectively denoted M. The proportions of the products of steps (1) and (2) are subject to readjustment, with concomitant adjustment of the H/OH ratio. This occurs directly by the bimolecular step

$$\text{OH} + \text{H}_2 \iff \text{H}_2\text{O} + \text{H}, \quad (7)$$

whose exothermicity in the forward direction, as above, is only +15 kcal/mole, and whose forward and reverse rates are both large and become nearly equal. Both (1) and (2) are kinetically second order in the energetic fragments and so both rates diminish quadratically as net recombination is accomplished at fixed density, or as density is diminished by expansion. Up to ca. 2400 K at the densities for which their rates are significant, these steps are substantially irreversible, and their rate coefficients diminish only mildly with increasing temperature.

In stoichiometric and fuel-lean compositions, step (3) and the complex paths formed by steps (4), (5), and (6) are comparatively important, and step (1) not so. The reaction-order and irreversibility characteristics of step (3) are similar to those of steps (1) and (2)
discussed above. The thermochemistry of HO$_2$ makes reversibility of step (4) a serious complication. Within the (4) - (5)/(6) sequences, step (4) is rate-limiting at high fragment fractions and recombination is first-order in O$_2$ and H-atom populations. Although excess O$_2$ is not consumed in proportion to the fragments, progressive recombination diminishes the H-atom population nonlinearly. Reversible step (4) becomes equilibrated and step (6) becomes rate-limiting. And the net recombination rate by the (4)-(6) sequence becomes seriously diminished as temperature is raised above ca. 2000 K, leaving step (3) to become the dominant path near 2500 K in fuel-lean compositions and step (2) in near-stoichiometric compositions.

**Hypersonic Flow Simulation**

Earlier we [2] have modeled numerically the kinetics and thermomechanics of premixed, quasi-one dimensional, time-steady streamline segments that simulate supersonic Hz/air combustion in a hypersonic ramjet. Of concern was the chemical basis of combustion efficiency. An undocumented Los Alamos code for finite-rate kinetics and thermochemistry, adapted to this application, was used.

Coupled engine/nozzle flow was simulated for a hypothetical vehicle flying at Mach 15 in air at $1.3 \times 10^5$ ft above the earth as a representative case. Stoichiometrically metered gaseous H$_2$ fuel from a lower temperature source was taken as mixed instantaneously with ram-compressed air at the initial station [3]. Static temperature and pressure of the mixed stream were 1463 K and 447 torr (59.5 kPa; 8.64 psia). Resulting internal axial stream velocity was $4.34 \times 10^3$ m/s.

For this base case, computed finite-rate reaction was followed through a 1-m long, constant-area combustor. Following ignition, near-equilibrium composition was reached at 2932 K, with 58% of the ideal combustion energy realized. Fragment species harbored the remaining 42%.

Next, expansion of the flow area beyond this 1-m station was modeled to an area sixteen times the combustor area over 1.5 m of further flow. Effects of selected area vs distance profiles were compared.
Computed static temperatures dropped from near 3000 K to near 1000 K. Computed composition began to shift toward a more complete energy-yield condition, but froze with only modest fractions of the remaining 42% realized.

This model scenario formed the base case for our present numerical examination of effects of added catalyst types in the early expansion.

**CATALYZED RECOMBINATION**

As potential catalysts for recombination, we may consider two classes:

(a) Substances that catalyze steps (1)–(4) as third bodies, M, with large rate coefficients; and

(b) Substances that introduce parallel paths analogous to the HO₂ sequence, (4)–(5)/(6), with such thermochemistry that, like O₂, they are regenerated and not irreversibly consumed.

Such catalytic substances can enhance the energy recovery through recombination early in the expansion of combustion products in which ideal combustion is stoichiometrically incomplete owing to too high a temperature for the combustion-stream pressure. They can do so profitably if, in the time of such early expansion, they enable a greater yield of chemical energy and increment of streamline thrust to be achieved than could alternatively be achieved from the combined influences of more complete equilibrium combustion and uncatalyzed early recombination realized from addition of a like mass of excess fuel or "inert" thermal ballast to the combustion flow.

As prospective catalysts we select representative substances from those volatile materials that are known to inhibit flames. These are recognized by their qualitative consequences of lower flame speeds in gaseous systems that include them as additives, and/or wider minimum channel dimensions for flame propagation. Their mode of
action is generally associated with diminished radical populations in
the ignition phase of combustion, where radicals (including the atomic
species H and O) function as carriers in chain-reaction sequences.
Paradoxically, the same agents and recombination mechanisms serve
to promote the completion of combustion from an intermediate com-
position in which ignition coupled with high temperature have pro-
duced a surplus of "intermediate" fragments. Since experience
teaches that reactions (1)–(4) have almost their largest rate coeffi-
cients with H₂O as the third body as with any known species, the
flame-inhibiting catalysts we are led to consider come from class (b)
above. Two chemical types of these catalysts are distinguished:
(i) nonmetals, either as atoms or low-valence oxides, and (ii) molecular
metal oxides.

**Nonmetal Oxide Catalyst**

Nitric oxide, NO, is a prototype catalytic substrate to which
H-atoms and also O-atoms and OH radicals each combine in a process
analogous to step (4), and will be abstracted in steps analogous to
(5)/(6). In each case the bond formed in the three-body step is analo-
gous in strength to the bonds in the HO₂ from step (4). Thus, subse-
quent abstraction by a second atom or OH radical to form a 100–
118 kcal/mole bond is exothermic, in the pattern of steps (5)/(6), and
NO is liberated to complete a homogeneous catalytic cycle. The proto-
type steps for fuel-rich hydrogen-air recombination are:

\[
\begin{align*}
\text{H} + \text{NO} + \text{M} & \leftrightarrow \text{HNO} + \text{M} & \text{(N4)} \\
\text{H} + \text{HNO} & \rightarrow \text{NO} + \text{H}_2 & \text{(N5)} \\
\text{OH} + \text{HNO} & \rightarrow \text{NO} + \text{H}_2\text{O} & \text{(N6)}
\end{align*}
\]

The full set of steps used in modelling, and their rate coefficients, are
conveniently surveyed elsewhere [4].
NO is not stable against atmospheric oxidation or physiologically benign enough to be a useful flame-retarding agent in room-temperature fire protection applications. Its role as a (generally undesirable) by-product of air-based combustion is well studied, however. Its presence in hypersonic propulsion streams is neither wholly avoidable nor dependent upon nonfuel material being carried in the vehicle for addition to the flow. Moreover, the behavior of NO as a recombination catalyst was directly studied early on \([5,6]\) in postilame gases from premixed, fuel-rich, atmospheric pressure \(H_2-O_2-N_2\) flat flames providing small, slowly decaying residual radical pools. In the 1600–2000 K temperature range so investigated, HNO is stable enough against dissociation that catalysis is pronounced. Recombination of the surplus fragments occurs unaccompanied by noticeable diminution of the artificially added \([\text{NO}]+[\text{HNO}]\) inventory through thermodynamically spontaneous but slower global reaction

\[
H_2 + \text{NO} \quad \rightarrow \quad H_2O + \frac{1}{2}N_2 .
\]

\([N7]\)

The catalytic behavior of NO in the hypersonic combustion situation we modeled differs from that in the flat flame in several respects, in consequence of (i) the higher combustion temperature \((2400 < T < 3000 \text{ K})\) we considered to precede expansion-induced recombination, and (ii) the significantly larger (forty-fold) fragment fraction (near 4\% of the total flow, including \(N_2\)) to be recombined. The major effect is significant interruption of the catalytic cycle by frequent reversal of the bond-forming step \((N4)\). The low net rate of \((N4)\) becomes rate-limiting even as the larger \(H\) and \(OH\) populations make the HNO lifetime in steps \((N5)/(N6)\) shorter than in the flat flame situation.

The second major difference, also primarily caused by the higher temperature range at which catalyzed recombination is needed in hypersonic combustion, is increased rates of the endothermic steps

\[
O + \text{NO} \quad \rightarrow \quad N + O_2
\]

\([N8]\)
of the extended Zeldovich chain. When that chain is completed by its rapid, exothermic step

\[ \text{H} + \text{NO} \rightarrow \text{N} + \text{OH} \]  \hspace{1cm} (N9)

there arises further need for recombination to accomplish reaction (N7).

**Metal Oxide Catalysts**

The other, and more promising class of recombination catalysts we have explored comprises partially oxidized forms of several metals, ranging in atomic weight from Mg to U. A survey was made [7] of twenty such metallic elements as part-per-million additives in atmospheric-pressure postflame gases near 1860 K. \( \text{H}_2\text{O}_2\text{N}_2 \) proportions were 3:1:6 and atom densities of \( 5 \times 10^{12} \text{ cm}^{-3} \) of each added metal were introduced as sprayed aqueous solution of a suitable salt. The largest catalytic effects [7], "2 orders of magnitude more effective than...NO...," occurred with the transition metals Cr, U, Sn and Mn. Similar catalysis also was found at 1860 K with the group II metals, Mg and the previously identified [8] heavier alkaline earths, Ca, Sr, and Ba. All these catalysts were further examined in hotter flames having lower proportions of \( \text{N}_2 \), up to temperatures above 2400 K, where catalysis by the alkaline earth metals was significantly diminished. But, [7] "for Sn, Cr, and U [there was] no definite trend either up or down [over the 1800-2500 K range]." This finding implies that these metals will not lose their catalytic efficiency for promotion of recombination in the temperature regimes found in hypersonic ramjet propulsion.

For the group II elements and some if not all of the transition metals, catalytic sequences analogous to steps (4) - (6) are established.
In these, the analogs of O$_2$ and HO$_2$ are respectively, the strongly bound diatomic metal monoxide and the corresponding monohydroxide. Electronic states of the hydroxide other than its most strongly bound, ground state have been implicated in the catalytic sequence. Also, catalysis by involatile oxide particles is an incompletely resolved possibility for some of the transition metals, including Cr and U.

The flame chemistry and spectroscopy are more extensively studied [9] in the case of tin, and we chose this metal as the additive for modeling prospective catalyzed recombination in hypersonic combustion. In particular, SnO was shown to be the predominant species indistinguishable from 100% of the tin inventory. Even so, representation of the empirical catalysis by added Sn in postflame gases by means of elementary steps and their rate coefficients is uncertain.

Bulewicz and Padley [7] report an empirical rate constant, $k'_{\text{cat}}$ for the global reactions

$$H + \text{H(OH)} + \text{SnO} \rightarrow \text{H}_2\text{(H}_2\text{O)} + \text{SnO} \quad (T1.2)$$

The $k'_{\text{cat}}$ in this paper expresses the incremental contribution to the H-atom removal rate after subtraction of the terms from the uncatalyzed mechanism, representing the combined effect of steps (1) and (2) with H$_2$O, N$_2$ etc., as $M$. The rate coefficient was found to be

$$k'_{\text{cat}} = 5 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

Allowance is included here for the stoichiometric factor of 2 between the rate of step (1) and the specific rate of reduction of the H-atom population. The mean of three $k'_{\text{cat}}$ values above 2000 K is adopted. If the global reactions (T1.2) are assumed to be the elementary reaction steps for the catalytic mechanism a rate constant $k_{1,\text{SnO}}$ of this magnitude is unrealistically large.

Nevertheless, to assess the effectiveness of tin as a catalytic additive we incorporated into our kinetics model the reactions (T1.2).
With the addition of only 0.1% mole-fraction SnO of the total flow we realized an increase in the ideal combustion energy yield from the noncatalyzed 58% to 79%. This dramatic result compares to the equilibrium constrained result of nearly 100%.

The foregoing value of \( k_{\text{cat}} \) is based on experience at \( \leq 10^{-3} \) H-atom fraction in the flame gases, whereas early expansion of hypersonic combustion gases from a condition near 2900 K involved H-atom fraction up to 40 times larger. The consequent rate terms are thus extrapolated in our model to \( \sim 10^{3} \) times larger magnitude. While this model indicated very strong catalysis its validity is uncertain.

As an alternative to using SnO as M in steps (1)-(4), the sequence:

\[
\begin{align*}
H + \text{SnO} + M & \quad \Leftrightarrow \quad \text{SnOH}\,^* + M \quad \text{(T4)} \\
H + \text{SnOH}\,^* & \quad \rightarrow \quad \text{SnO} + H_2 \quad \text{(T5)} \\
\text{OH} + \text{SnOH}\,^* & \quad \rightarrow \quad \text{SnO} + H_2O \quad \text{(T6)}
\end{align*}
\]

has been postulated \([7, 9]\). The superscript \( * \) denotes an electronically excited state of the monohydroxide molecule, SnOH.

Pursuing this catalytic sequence, steps (T4)-(T6) to represent the \( k_{\text{cat}} \) in Ref. 7 paper, the deduced the equilibrium-constant ratio was

\[
K_4 = \frac{k_{T4}}{k_{T4}} = 3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}
\]

and the rate coefficient was

\[
k_{T5} = 2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.
\]
When we have estimated individual values of $k_{T4,M}$ and $k_{T4,M}$ for $H_2O$ and $N_2$, and $M$ we find catalytic rates under hypersonic combustion conditions that are understandably smaller than by the $k_{cat}$ above, but not insignificant.

CONCLUSION

The more complete existing information on nonmetal oxides indicates that catalytic enhancement of combustion power by adding intentionally these materials will be unattractive, but the effects of constituents such as NO formed naturally from combustion in air are not negligible. However, the effects we predict based on the available literature data on metal oxides is encouraging. We conclude that further experimental investigation of volatile metallic additives as catalyst for recombination of $H_2O$ fragments at high temperature, $T > 2400$ K, is advisable to advance the prospect of efficient, kinetically controlled enhancement of power for propulsion of hypersonic ramjets in circumstances where combustion would otherwise be thermochemically complete.
REFERENCES


EFFECTS OF VISCOSITY AND TEMPERATURE ON APPLIANCE PERFORMANCE IN RESIDENTIAL OIL COMBUSTION

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CANMET. Energy, Mines and Resources Canada.
Ottawa. Canada. K1A 0G1

INTRODUCTION

A research program on combustion performance evaluation of Canadian middle distillates was carried out at the Combustion and Carbonization Research Laboratory. The program was initiated in response to the needs of the oil industry as well as the standard writing bodies for better fuel quality specifications. The combined effects of industry’s effort to maximize the product yield from a crude barrel and the increasing demand on light distillates created the increased use of lower quality products for heating. In Canada, where an abundance of oil sands bitumen and heavy fuels are available, the use of distillates processed from such unconventional sources presents a practical solution to increasing energy demand and declining conventional resources. The effects of these lower quality products on appliance performance must be examined and technologies developed to ensure safe and efficient utilization of the fuels in existing appliances. The standard writing bodies require such information as well to update the existing specifications as required as the quality of the products and the equipment requirements change from time to time. Data from this program are being used to establish correlations fuel properties and combustion characteristics of various Canadian distillate fuels. This paper describes information that demonstrate the effects of fuel viscosity on particulate emissions generated during the transient operation of a residential oil burner.

EXPERIMENTAL SECTION

Fuel variety

Fuel oils were contributed by various Canadian oil companies. The origin of crudes and process vary depending on the company and location. Special blends were prepared in the laboratory to include fuels with a wide range of viscosities. A particular effort was made to keep other variables at a constant value especially aromaticity. All blends contained fuels of different origin and do not necessarily represent the same fuel matrix.
Fuel analysis

Chemical and physical properties of the fuels were determined using standard ASTM techniques. Aromaticities of the fuel were determined by the proton nuclear magnetic resonance (1HNMR) method. The 1HNMR spectra were obtained on a Varian model EM-390 spectrometer operated at 90 MHz. The samples were prepared by mixing the oil with chloroform-d$_1$ in a 50/50 volume ratio and a drop of Me$_4$ Si was added as a reference. Aromaticities of the fuels were calculated from hydrogen intensities using the method of Muhl et.al (1).

Combustion experiments

Short term combustion experiments were carried out using the procedure developed at the Combustion and Carbonization Research Laboratory (2). The experimental procedure simulated the actual usage pattern of residential oil heating in Canadian homes. A typical experimental run started with an initial burner startup (cold start) which lasted one hour (steady state), immediately followed by five consecutive 10 minutes on /10 minutes off, cyclic operations. Flue gas emissions and temperatures at specified locations of the test rig were continuously monitored over the entire run. The following experimental equipment and operating conditions were used.

<table>
<thead>
<tr>
<th>Fuel temperature:</th>
<th>15°C set as required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle oil temperature:</td>
<td>100 psi</td>
</tr>
<tr>
<td>Fuel pump pressure:</td>
<td>0.75 US gph with 80 spray angle</td>
</tr>
<tr>
<td>Oil nozzle:</td>
<td>Set to obtain a No 2 smoke at steady state</td>
</tr>
<tr>
<td>Combustion air:</td>
<td>15 ± 1°C</td>
</tr>
<tr>
<td>Cold air return temperature:</td>
<td>Beckett burner and Aero AFC2</td>
</tr>
<tr>
<td>Burner and retention head:</td>
<td>Forced air type. Brock model LO-1M, 74,000-120,000 Btu/h, with concentric tube type heat exchanger.</td>
</tr>
<tr>
<td>Furnace:</td>
<td>1 mm (0.04 in) of water column</td>
</tr>
</tbody>
</table>

The fuel temperature was kept constant at 15 °C in a fuel conditioner that was cooled by a circulating coolant. A thermocouple was inserted into the centre of the nozzle adapter at a closest possible position to the nozzle tip. The oil temperature at discharge was determined using this thermocouple. That temperature was controlled by cooling the combustion chamber and burner with a blast of chilled air. The nozzle temperature was held between 17 and 19°C for all fuels. Each fuel was tested for a minimum of three times and average values were reported.
Measurement of particulate emissions

Particulates, mainly soot, in the flue gas stream were determined using a commercial smoke opacity meter (Celesco model 107). The meter uses a light attenuation principle and is normally used for determining smoke in diesel engine exhaust gases. The instrument was installed vertically, in line with the furnace flue pipe. The opacity % reading from the meter was continuously recorded on a strip chart recorder to capture the entire soot production profile at each transient operation. Area under the peak of each operation was reported as area in square inch per transient cycle.

RESULTS AND DISCUSSION

Fuel variety

Several Canadian oil companies contributed fuels of different origins to this quality evaluation program. These included products from conventional crudes, both Canadian and imported, and synthetic crudes processed from oil sands bitumen and heavy oils. Several special blends had to be prepared in house to obtain fuels with specific qualities. Results have shown that fuel viscosity and aromatics show the strongest influence on oil burner performance (3). This study was dedicated to examine the fuel viscosity effects on combustion performance and required fuels with varying viscosities but with similar aromatic contents. The current CGSB requirement for No. 2 heating fuels is a minimum of 1.4 and a maximum of 3.6 centi stoke or millimetre/second at 40 °C. Fuels with a range of viscosities 1.8 to 5.1 at 38°C (100°F) were included in this study.

Chemical and physical properties of the fuels

Each fuel was analyzed for aniline point, aromatics, aromaticity, calorific value, cloud point, density, distillation range, flash point, pour point, ramsbottom carbon, viscosity, water and residue, and ultimate analysis using ASTM (American Society for Testing and Materials) and CGSB (Canadian General Standards Board) standard methods. The fluorescent indicator adsorption method (FIA) presents operational problems for fuels with final boiling points higher than 315 °C and colored fuels in determining the fuel aromatic content. The 1HNMR technique provides the percent ratio of the aromatic carbons to the total number of carbons present in an average molecule that represent a fuel. Table 1 reports some of the analysis data of 15 fuels included in the experimental program.
Particulate emissions from combustion

Performance of fuels are rated in terms of several combustion characteristics including burner ignition behaviour, flame characteristics, potential burner failure, appliance efficiency, heat exchanger corrosion and gaseous and particulate emissions. Poor fuel quality is associated with poor appliance performance and excessive emissions of incomplete combustion products such as particulates, carbon monoxides, and hydrocarbons. Data indicate that carbon monoxide and hydrocarbon emissions exhibit the same trend as particulate emissions. The discussion in this paper is focused on the performance rating as reflected by the generation of particulates.

The commercial smokemeter used was found to be sensitive to particulates equivalent to or higher than smoke number 5, when tested with a commercial Bacharach smoke tester (industry's standard smoke test equipment). The meter has to be especially calibrated for this application.

Results indicate that particulates generated during the cold temperature burner start (cold start) are significantly higher than those from on/off cyclic operations (warm start). This difference is mainly due to the temperature difference at which combustion of the oil takes place. The cold start temperature was set between 17°C and 19°C, based on the actual readings found in homes located in central Canada (17 - 24°C). The nozzle oil temperature increased to between 45°C and 70°C during cyclic operations. A significant observation was made in that lower quality fuels generated excessive soot at cold start but produced near normal levels (compared to within-spec heating fuel) at warm start.

Figure 1 shows the smoke opacity profile recorded from a commercial within-spec heating fuel. The first peak represents the cold start and the peak at the end of one hour run represents the burner shutdown. It can be compared to the Figure 2 profile from combustion of a fuel with high aromatics and a viscosity higher than specifications. The duration of time taken for dissipation of soot from the furnace exit also serves as a good indicator of performance. Table 2 represents data from 15 test fuels. As indicated by data in table 1, aromaticity of fuels is reasonably similar with the exception of Fuels 14 and 15. Both have high fuel aromatics but Fuel 14 has higher viscosity (beyond maximum 3.6 c St at 40°C) than Fuel 15 (within-spec). Data in table 2 indicate an increase in both area under the smoke opacity peak and smoke dissipation time with increased fuel viscosity. Figure 3 is the graphical representation. The high value for Fuel 14 resulted from high fuel viscosity as well as high fuel aromatics. However, Fuel 15 exhibits only a higher than normal value (than those from Fuels 3, 4, 5), despite the fact that it has
a similarly high aromatics as in Fuel 14. It appears that higher than spec viscosity can be tolerated provided that fuel aromatics are reasonably low. There is no specific specification for fuel aromatics in place but most of the commercial furnace fuels have below 40 volume percent (about 25% aromaticity). A similar example can be demonstrated using data from Fuels 10 and 11. The fuel density also plays a partial role. Although there is a general positive trend between viscosity and density, the correlation is not always true. If higher than specifications viscosities are to be used, it is essential that both aromatics and density be kept at low levels.

Figure 4 represents the effect of oil temperature at the nozzle on particulate emissions of Fuel 15. It is similar to the viscosity - emission relation, since the oil temperature directly controls the viscosity. It can be compared to Figure 5 showing the viscosity - emission relation of a commercial furnace fuel (Fuel 3). The viscosity of Fuel 3 was determined at different temperatures and a temperature-viscosity calibration line was developed. Particulate emissions of Fuel 3 determined at different cold start combustion temperatures are shown in Figure 5. This fuel was tested to provide information on the cold start behaviour of commercial furnace fuels at cold regions of Canada. There are certain areas of area where the basement temperatures are low enough to have an oil combustion temperature of 50°C. In such cases, the viscosity of a commercial fuel suitable for an average climate could increase to its critical value at which poor combustion will result (3). Data suggests that a fuel with viscosity about 2.5 cSt at 38°C could be used in locations where the coldest basement temperature is about 10°C, without any negative effects.

It can be concluded from this study that increasing fuel viscosity has a strong positive influence on incomplete combustion products. The combustion performance of lower grade fuels can be improved and manipulated to advantage if other dominating fuel properties can be controlled.

ACKNOWLEDGEMENT

The authors thank D.E. Barker for combustion experiments, F.W. Wigglesworth for analytical instrumentation and D.C. Post for graphics.

REFERENCES

Fig. 1. Opacity profiles of cold start and shut down from a steady state furnace fuel.

Fig. 2. Opacity profiles of cold start and shutdown from a steady state firing a high viscosity, high aromatic fuel.

Table 1. Fuel variety and properties

<table>
<thead>
<tr>
<th>Fuel ID &amp; type</th>
<th>Viscosity, c St @ 380C</th>
<th>H/C ratio</th>
<th>Aromaticity, % by 1H NMR</th>
<th>Density, kg/L @500C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. special blend</td>
<td>1.88</td>
<td>1.806</td>
<td>15</td>
<td>0.840</td>
</tr>
<tr>
<td>2. winter diesel</td>
<td>2.09</td>
<td>1.802</td>
<td>16</td>
<td>0.845</td>
</tr>
<tr>
<td>3. furnace fuel</td>
<td>2.48</td>
<td>1.782</td>
<td>16</td>
<td>0.844</td>
</tr>
<tr>
<td>4. furnace fuel</td>
<td>2.52</td>
<td>1.748</td>
<td>20</td>
<td>0.855</td>
</tr>
<tr>
<td>5. furnace fuel</td>
<td>2.68</td>
<td>1.732</td>
<td>21</td>
<td>0.864</td>
</tr>
<tr>
<td>6. special diesel</td>
<td>2.90</td>
<td>1.663</td>
<td>24</td>
<td>0.879</td>
</tr>
<tr>
<td>7. special blend</td>
<td>3.00</td>
<td>1.712</td>
<td>21</td>
<td>0.864</td>
</tr>
<tr>
<td>8. light gas oil</td>
<td>3.26</td>
<td>1.798</td>
<td>21</td>
<td>0.860</td>
</tr>
<tr>
<td>9. special blend</td>
<td>3.39</td>
<td>1.744</td>
<td>23</td>
<td>0.864</td>
</tr>
<tr>
<td>10. special blend</td>
<td>4.09</td>
<td>1.746</td>
<td>18</td>
<td>0.872</td>
</tr>
<tr>
<td>11. special blend</td>
<td>4.24</td>
<td>1.766</td>
<td>11</td>
<td>0.881</td>
</tr>
<tr>
<td>12. special blend</td>
<td>4.87</td>
<td>1.768</td>
<td>11</td>
<td>0.883</td>
</tr>
<tr>
<td>13. special blend</td>
<td>5.12</td>
<td>1.740</td>
<td>18</td>
<td>0.884</td>
</tr>
<tr>
<td>14. light cycle oil</td>
<td>3.60</td>
<td>1.378</td>
<td>40</td>
<td>0.926</td>
</tr>
<tr>
<td>15. special blend</td>
<td>2.74</td>
<td>1.406</td>
<td>42</td>
<td>0.923</td>
</tr>
</tbody>
</table>

Table 2. Particulate emissions from fuels with different viscosities

<table>
<thead>
<tr>
<th>Fuel Viscosity, c St @ 380C</th>
<th>Area 1, sq.in.</th>
<th>Time 2, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1.88</td>
<td>0.21</td>
<td>15</td>
</tr>
<tr>
<td>2. 2.09</td>
<td>0.08</td>
<td>12</td>
</tr>
<tr>
<td>3. 2.48</td>
<td>0.15</td>
<td>22</td>
</tr>
<tr>
<td>4. 2.52</td>
<td>0.13</td>
<td>24</td>
</tr>
<tr>
<td>5. 2.68</td>
<td>0.26</td>
<td>29</td>
</tr>
<tr>
<td>6. 2.90</td>
<td>0.31</td>
<td>44</td>
</tr>
<tr>
<td>7. 3.00</td>
<td>0.16</td>
<td>12</td>
</tr>
<tr>
<td>8. 3.26</td>
<td>0.16</td>
<td>42</td>
</tr>
<tr>
<td>9. 3.39</td>
<td>0.73</td>
<td>55</td>
</tr>
<tr>
<td>10. 4.09</td>
<td>3.65</td>
<td>180</td>
</tr>
<tr>
<td>11. 4.24</td>
<td>0.35</td>
<td>120</td>
</tr>
<tr>
<td>12. 4.87</td>
<td>5.36</td>
<td>325</td>
</tr>
<tr>
<td>13. 5.12</td>
<td>8.56</td>
<td>465</td>
</tr>
<tr>
<td>14. 3.60</td>
<td>52.30</td>
<td>750</td>
</tr>
<tr>
<td>15. 2.74</td>
<td>0.31</td>
<td>44</td>
</tr>
</tbody>
</table>

1. area under the opacity peak
2. Time for smoke to dissipate

Fig. 3. The effects of viscosity on particulate emissions
Figure 4. Effect of temperature on particulate emissions. Fuel 15.

Figure 5. Effect of viscosity on particulate emissions. Fuel 3.
Environmental concern over the safe disposal of toxic organic wastes has led to the emergence of the field of incineration as one of the more controversial and exciting applications of the combustion sciences [1]. A significant fraction of hazardous organic wastes are chlorinated hydrocarbons (CHCs) [2]. The presence of chlorine brings a number of complications to the understanding of the incineration process beyond that usually addressed in combustion research.

For a CHC designated by C\textsubscript{y}H\textsubscript{x}Cl\textsubscript{z}, the overall equilibrium combustion stoichiometry can be defined for $y > z$:

$$C\textsubscript{y}H\textsubscript{x}Cl\textsubscript{z} + (x + (y - z)/4) O_2 = x CO_2 + z HCl + (y - z/2) H_2O.$$

For $y < z$, the formation of molecular chlorine (Cl\textsubscript{2}) must be considered:

$$C\textsubscript{y}H\textsubscript{x}Cl\textsubscript{z} + x O_2 = x CO_2 + z HCl + ((z - y)/2) Cl_2.$$

Numerous full-scale tests and thermodynamic calculations have clearly indicated that the nature and quantity of organic compound emissions from toxic waste incinerators are not thermodynamically controlled, actual emissions being greater than $10^5$ times that predicted from equilibrium [4]. Due to their toxicity, there is particular concern over the emissions of chlorinated products of incomplete combustion (PICs).

Simple conceptual and more complex computer models suggest that kinetic factors including temperature, time at temperature, and reaction atmosphere in the post-flame, or thermal zones, of full-scale incinerators control the emission of organic compounds from such systems [5-7]. These models further indicate that hazardous wastes entering the flame zone are completely oxidized and only the small fraction that does not pass through this zone may undergo incomplete reaction. Various excursions may cause a small fraction of the waste to circumvent the flame zone [6,7]. Once in the post-flame zone, high-temperature thermal decomposition kinetics control the rate of waste destruction and the rate of formation and destruction of organic byproducts.

Emissions from full-scale incinerators are generally several orders of magnitude higher than those calculated using rate parameters obtained from laboratory-scale experiments simulating the oxidative reaction conditions in the post-flame zones of such systems [6,8]. This result suggests that oxygen-starved reaction pathways may be responsible for most organic emissions since the rate of destruction of the parent is significantly slowed and the rate of organic byproduct formation is substantially increased [8-10]. Thus, although incinerators operate under oxygen-rich conditions, oxygen-starved pockets may exist in the system due to locally poor mixing conditions. Consequently, laboratory-scale flow reactors appear to be particularly well suited for the evaluation of the fuel-rich thermal decomposition behavior of CHCs.
To build a database of the possible reaction mechanisms involved in the formation of CHC emissions under oxygen-starved reaction conditions, we have initiated a program to evaluate the high-temperature thermal decomposition behavior of different classes of CHCs using fused silica flow reactor thermal instrumentation. Our initial study involved an analysis of the simplest of CHCs, the chlorinated methanes, as pure compounds and as mixtures of varying elemental composition \([HCl = 3.0]\). The most important finding was the observation of significant yields \((\geq 0.1 \text{ mole} \%)\) of higher-molecular-weight, thermally stable, unsaturated CHCs, e.g., hexachlorobenzene \((C_6Cl_6)\), for \(H:Cl\) ratios less than 1.0 under oxygen-starved \((\phi = 3.0)\) reaction conditions.

As a consequence, we have begun a study of \(C_2\)-CHCs, with particular interest on the analysis of pentachloroethane \((C_5HCl_5)\), hexachloroethane \((C_6HCl_6)\), trichloroethylene \((C_2HCl_2)\), tetrachloroethylene \((C_4HCl_4)\), and dichloroacetylene \((C_2Cl_2)\). These saturated and unsaturated \(C_2\)-chlorocarbons have been observed as intermediates in the high-temperature oxygen-starved decomposition of chloroform, carbon tetrachloride, and chloromethane mixtures \((H:Cl = 0.2)\) \([11,12]\). The formation of these compounds has been hypothesized to be an important step in reaction channels leading to chlorinated aromatics and chlorinated polynuclear aromatic hydrocarbons (PNAs) \([11-13]\). These high-molecular-weight organic compounds have been detected in stack gases of full-scale incineration systems. Such emissions are unacceptable because of their potential toxic effects on human health and the environment.

**Experimental**

Kinetic studies were conducted using various isothermal fused silica flow reactors equipped with in-line GC and GC/MS analytical systems \([14,15]\). These closed continuous thermal instrumentation systems permit quantitative data to be obtained expediently without errors associated with batch sampling and lack of true quantitative transport. A block diagram of one such system, the System for Thermal Diagnostic Studies (STDS) is shown in Figure 1a; a cross-section view of the thermal reactor is shown in Figure 1b.

The reactor is geometrically configured as a helical tube 500 cm long with an internal diameter of 0.17 cm. The geometry of the reactor produces a laminar gaseous flow which exhibits a nearly square wave thermal pulse with a very narrow, near-Gaussian residence time distribution, thus making this reactor ideally suited for reaction kinetic studies. The thermal reactor consists of a relatively inert, high-temperature fused silica material. However, one of the compromises of the precise time/temperature control of this reactor is the corresponding large surface to volume ratio \((23.5 \text{ cm}^{-1})\). Using gas collision theory, we have evaluated the relative importance of heterogeneous surface decomposition as compared to homogeneous thermal decomposition for several hydrocarbons and CHCs for which experimental rate data have been previously estimated. Activation energies for heterogeneous decomposition were estimated by assuming the wall reaction rate represented 100% of the experimental reaction rate at a temperature corresponding to the onset of chemical reaction.

Ratios of rate constants and destruction efficiencies \((DE)\) were calculated at temperatures corresponding to 50%, 90%, and 99% decomposition for 2 hydrocarbons and 6 CHCs. With the exception of benzene \((C_6H_6)\) and dichloromethane \((CH_2Cl_2)\), the results indicated that heterogeneous decomposition accounted for less than 10% of the measured decomposition at overall decomposition levels of 90 and 99%. These calculations imply that, at low temperatures, wall collisions may initiate...
the radical chain processes that likely dominate CHC decomposition. However, at higher temperatures, due to the much larger activation energies for homogeneous (-55.0 to -100 kcal/mole) as compared to heterogeneous (-25.0 to 35.0 kcal/mole) decomposition, gas-phase reactions dominate initiation processes and radical chain processes in general.

Following thermal exposure, the effluent is quenched in a heated (250°C) fused silica transfer conduit which connects the reactor to the thermal trapping/gas chromatographic assembly. Leading to and from this assembly are separate, thermally programmable transfer paths designed to produce nonreactive quantitative transport of organic substances. Migrating effluent species from the reactor are then trapped at -60°C and axially focused at the head of the GC column for subsequent analysis.

In this manuscript, we report the results of two different sets of experiments. Pure CCl₂ thermal decomposition behavior of the chlorinated ethanes and chlorinated ethenes was evaluated in multi-component organic mixtures of constant elemental composition (C₅H₃Cl) under oxygen-starved conditions. The constant elemental composition produces an essentially invariant radical pool which allows the evaluation of stability of the CHCs under realistic conditions. The experimental approach will be presented in more detail in future publications.

Results

The thermal stability data for the chlorinated ethane and chlorinated ethene mixture experiments are summarized in Figures 2 and 3 and Table 1. For the chlorinated ethanes, three initiation pathways are plausible: (1) concerted 4-center elimination of HCl, (except for C₅Cl₆); (2) carbon-chlorine bond rupture; and (3) carbon-carbon bond rupture. In addition, the reactive radicals formed by the latter two mechanisms can attack the parent compound and abstract available hydrogen atoms, resulting in an apparent decomposition rate as much as 2-3 times greater than the unimolecular initiation rate. In all cases, a major product is expected to be the olefin corresponding to loss of HCl by one of these mechanisms. This is even the case for C₅Cl₆ with a hypothetical mechanism involving C-Cl β-bond rupture following initial C-Cl bond rupture. Our mixture studies generally result in a faster rate of decomposition compared with pure compound flow reactor and shock tube studies reported in the literature, presumably due to secondary chain reactions [16-20]. Important decomposition rate parameters which include data reported in the literature and thermochemical estimates are given in Table 2. Both theory and experiment suggest that for the homologous series, there is a trend of decreasing stability with increasing chlorination. Carbon-carbon and carbon-chlorine bond rupture become more favorable with increased chlorination due to weakening of these bonds while the rate of HCl elimination is less sensitive. When comparing isomers, (e.g., 1,1,1-trichloroethane vs 1,1,2-trichloroethane), the isomer with more chlorines on a single carbon decomposes more rapidly. This may be influenced by weaker C-Cl and C-C bonds and a greater reaction path degeneracy for HCl elimination.

The chlorinated ethylenes are 200-300°C more stable than the chlorinated ethanes. These compounds increase in stability as chlorine substitution increases (see Table 1 and Figure 3). This suggests a dominant decomposition mechanism involving hydrogen atom abstraction by reactive radicals such as Cl atoms. C₅Cl₄, which contains no H atoms, is the most stable of the series, and decomposition by the
endothermic (\(\Delta H^\circ \approx 27.5 \text{ kcal/mole}\)) pathway of Cl abstraction by Cl to form Cl\(_2\) is not significant at the temperatures of our experiments.

Alternative decomposition pathways for the chloroethenes include HCl elimination and chlorine displacement by hydrogen atoms. Shock tube data from the literature for C\(_2\)H\(_2\)Cl suggest that HCl elimination is too slow to account for all of the observed rate of destruction [21]. Cl\(_2\) elimination for tetrachloroethylene seems even more unlikely due to its greater endothermicity (\(\Delta H^\circ \approx 53.5 \text{ kcal/mole}\)). Cl displacement by H has been experimentally demonstrated to be a viable mechanism for pyrolytic decomposition of chlorinated aromatics and is a potential destruction mechanism for chlorinated olefins [10]. However, the trend of increased stability with increasing chlorine content in our mixture studies does not support this pathway as the principal mechanism of destruction of the chloroethenes. The relative importance of H abstraction and Cl displacement mechanisms for these compounds has not yet been established.

These mixture studies have not addressed product formation; however, previous flow reactor studies of chloroform, carbon tetrachloride, and premixed flat-flame studies of trichloroethylene have shown that chlorinated olefins and olefinic radical species may be key intermediates in the formation of higher-molecular-weight chlorinated aromatic species [11-13,23]. As such, it appears important to study the chemistry of these intermediates more thoroughly.

The oxygen-starved thermal decomposition profile of C\(_2\)Cl\(_4\) is presented in Figure 4. The results indicate that this compound is very stable (\(T_{99.2} = 980^\circ C\)) under the conditions studied with measurable quantities (0.007%) persisting at the highest temperatures studied (1050^\circ C). Of the two compounds detected as PICs, hexachlorobenzene (C\(_6\)Cl\(_6\)) exhibited the greatest yields (-11% at 950 and 1050^\circ C) and was the most thermally stable. Carbon tetrachloride (CCl\(_4\)) was produced in lower yields and was 99.9% destroyed at 950^\circ C. It is probable that C\(_2\)Cl\(_3\) and Cl\(_2\) were produced as well in the thermal decomposition experiments; however, mass spectral data acquisition limitations precluded the detection of these products.

Comparison of the results of this pure compound study with previous flow reactor mixture experiments under fuel-rich conditions provides insight into possible C\(_2\)Cl\(_4\) decomposition pathways. Under hydrogen-rich mixture conditions, the formation of high yields of C\(_2\)HCl\(_3\) was observed indicating the importance of a mechanism involving H displacement of Cl atoms. Under pure compound conditions, the absence of hydrogen precludes such a mechanism. The types of products shown in Figure 4 suggest that C-Cl bond fission followed by reactions of C\(_2\)Cl\(_3\) radicals plays important roles in destruction of C\(_2\)Cl\(_4\).

We have previously proposed a mechanism for formation of C\(_2\)Cl\(_4\) from chloroform, which involves Cl displacement from C\(_2\)Cl\(_4\) (formed as an intermediate from chloroform) via reaction 1 [11-13]:

\[
\text{C}_2\text{Cl}_4 + \text{C}_2\text{Cl}_4 \rightarrow \text{C}_4\text{Cl}_6 + \text{Cl} \\
\text{(Rxn 1)}
\]

Hexachlorobutadiene (C\(_6\)Cl\(_6\)) has been shown in our lab to rapidly decompose via C-Cl bond rupture to form the resonance stabilized pentachlorobutadienyl radical (C\(_5\)Cl\(_5\)) which can then react with dichloroacetylene (C\(_2\)Cl\(_2\)) to form C\(_6\)Cl\(_6\) via reaction 2.

\[
\text{C}_4\text{Cl}_6 + \text{C}_2\text{Cl}_2 \rightarrow \text{C}_6\text{Cl}_6 + \text{Cl} \\
\text{(Rxn 2)}
\]
A possible route of formation of CC\(_4\) is chlorine addition to C\(_2\)Cl\(_4\) to form C\(_2\)Cl\(_5\), followed by \(\alpha\)-bond fission to form CC\(_2\) and CCl\(_3\), which can subsequently recombine with Cl atoms to form CC\(_4\). \(\beta\)-bond fission of C\(_2\)Cl\(_5\) to reform CCl\(_4\) is likely a faster reaction, and indeed there is evidence for reformation of CCl\(_4\) as indicated by the knee in the decomposition curve at 950°C (see Figure 4).

We were intrigued by the possibility that reaction 1 may be faster than its hydrocarbon analogue which has been proposed as a key reaction in soot and PNA formation in fuel-rich hydrocarbon flames.[24] The general scheme for activated complex reactions was used to perform a Quantum RRK (QRRK) calculation [25]:

\[
\begin{align*}
C_2Cl(H)_3 + C_2Cl(H)_4 & \overset{k_1}{\longrightarrow} \overset{k_2}{\longrightarrow} C_4Cl(H)_7 \\
& \ket{\beta k_3} \\
& \longrightarrow C_4Cl(H)_6 + Cl(H)
\end{align*}
\]

If \(k_1\) is rate-limiting, the stabilization reaction involving the chlorinated species may be facilitated by the following resonance structure

\[
\begin{align*}
\text{Cl} & \quad \overset{\text{Cl}}{\text{Cl}} \\
\text{Cl} \quad \overset{\text{Cl}}{\text{C}} \quad \overset{\text{C}}{\text{Cl}} \\
\text{Cl} & \quad \overset{\text{Cl}}{\text{Cl}} \\
\text{Cl} & \quad \overset{\text{Cl}}{\text{Cl}} \\
\text{Cl} & \quad \overset{\text{Cl}}{\text{Cl}}
\end{align*}
\]

which is not possible for the hydrocarbon analogue. If \(k_2\) is rate-limiting, the chlorocarbon reaction is facilitated by the displacement of chlorine which has a lower bond energy (D\(_{0}\)(C-Cl) = 85 kcal/mole) than hydrogen in the hydrocarbon (D\(_{0}\)(C-H) = 108 kcal/mole).

Rate constants for the hydrocarbon reaction were estimated from the literature [25]. The rates for \(k_1\) and \(k_2\) were assumed to be the same for both hydrocarbon and chlorocarbon analogues. \(A_0\) was estimated via transition state theory for the chlorocarbon reaction and \(E_c^*\) was estimated by assuming a linear relationship between activation energy and bond dissociation energy. Using the same rate for \(k_1\) and \(k_2\) for the chlorocarbon and hydrocarbon was considered a conservative method of evaluating the effect of chlorine substitution in displacement reactions. One could argue that the chlorocarbon addition step, \(k_1\), is slower due to the inductive destabilizing effect of chlorine; however, since radicals are not charged species, they do not respond to inductive effects as fully as to electrophilic attack by cations. Thus, we feel that resonance stabilization effects of chlorine may dominate. The results in Figure 5 confirm that the displacement reaction is faster at all temperatures for the chlorocarbon system. This is consistent with our findings in the chloromethanes, where relatively large yields of C\(_2\) and aromatic products were seen from chloroform (CHCl\(_3\)) and CCl\(_4\), but not observed at all from chloromethane (CH\(_3\)Cl) and dichloromethane (CH\(_2\)Cl\(_2\)).

The experimental and theoretical studies presented in this manuscript suggest that chlorinated hydrocarbons may be particularly prone to formation of complex, potentially toxic, reaction byproducts. A systematic, detailed kinetic and mechanistic study of the reactions of these compounds, particularly the C\(_2\)-olefins and acetylenic compounds is indicated.
ACKNOWLEDGMENT: We gratefully acknowledge the efforts of J. Kasner for performing the QRRK calculations and of our Project Officer, Dr. C. C. Lee for his advice and support.

CREDIT: This research was partially supported by the US-EPA under Cooperative Agreement CR-813938.

REFERENCES


### TABLE 1

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<td>1,1-Dichloroethane</td>
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<tr>
<td>1,1,1,2-Tetrachloroethane</td>
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<td>1,1,2,2-Tetrachloroethane</td>
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<td>Pentachloroethane</td>
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Table 2a. Decomposition Rate Parameters—Chloroethanes

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<td>17.5</td>
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<td>87.6</td>
<td>17.4</td>
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<tr>
<td>1,1,1-C3H3Cl3</td>
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<td>85.9</td>
<td>12.1</td>
<td>-</td>
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<tr>
<td>1,1,2-C3H3Cl3</td>
<td>-</td>
<td>85.5</td>
<td>12.1</td>
<td>-</td>
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<tr>
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<td>14.8</td>
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<td>13.1</td>
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<th>C-C</th>
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<td>NA</td>
<td>-21.2</td>
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Table 2b. Decomposition Rate Parameters—Chloroethanes

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<tr>
<th>Compound</th>
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<th>HCl Elim.</th>
<th>Cl Disp.</th>
<th>H abst. by Cl [b]</th>
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<td>-19.1</td>
<td>-</td>
</tr>
<tr>
<td>1,1-C2H4Cl2</td>
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<td>28.8</td>
<td>-15.8</td>
<td>-</td>
</tr>
<tr>
<td>1,2-C2H4Cl2</td>
<td>-</td>
<td>28.1</td>
<td>-15.1</td>
<td>-</td>
</tr>
<tr>
<td>1,1,2-C3H3Cl3</td>
<td>-</td>
<td>27.6</td>
<td>-21.5</td>
<td>3.5</td>
</tr>
<tr>
<td>1,1,2-C3H3Cl3 [l]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.8</td>
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<tr>
<td>1,1,1,2-C4H2Cl</td>
<td>-</td>
<td>27.6</td>
<td>-21.5</td>
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<td>C2HCl5</td>
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<td>C2Cl6</td>
<td>78.0</td>
<td>69.1</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Legend:

[a] Decomposition pathways from left to right are unimolecular C-Cl bond fission, C-C bond fission (chloroethanes only), 4-center HCl elimination, and bimolecular H abstraction by OH, and Cl displacement by H (for the chloroethanes only).

[b] Thermodynamic data were obtained from one of the following sources:
1. Reference 27
2. Reference 20

[c] Except where noted, Arrhenius A factors were calculated by transition state theory. Arrhenius Ea's were calculated by subtracting 0.5RT from the reaction enthalpy. In the absence of reaction enthalpies, Ea's were estimated by comparison with similar compounds. For 1,1,2-trichloroethane, 1,1,2-ltrachloroethane, and pentachloroethane, Arrhenius parameters reflect fission of the weaker C-Cl bonds.

[d] Except where noted, Arrhenius A factors were calculated by transition state theory. Ea's were estimated by comparison with similar compounds.

[e] Rate coefficients reflect H abstraction from highest chlorinated carbon unless otherwise noted.

[f] 4-center HCl elimination from 1,1,2-trichloroethane can occur by two pathways, with different reaction enthalpies.

[g] Beta-H abstraction.
Figure 1a. Schematic Diagram of the System for Thermal Diagnostic Studies.

Figure 1b. Cross-sectional schematic of helical tubular reactor.
Figure 3. Thermal decomposition curves for the chlorinated ethenes. Fuel/oxygen equivalence ratio = 3.0, mixture elemental composition = $C_3H_3Cl$, $t_r = 2.0$ s, total organic concentration = $4 \times 10^{-3}$ moles/L.
Figure 4. Thermal decomposition profile for tetrachloroethene. Fuel/oxygen equivalence ratio = 3.0, $t_r = 2.0$ s, $[C_2Cl_4] = 4 \times 10^{-3}$ moles/L.

Figure 5. Predicted effect of temperature upon reaction 1 for both hydrogen and chlorine analogues. $P = 1$ atm, log $A(H) = \log A(Cl) = 11.2$, $E_1(H) = E_1(Cl) = 7.3$, log $A_1(H) = \log A_1(Cl) = 12.7$, $E_2(H) = E_2(Cl) = 27.8$, log $A_2(H) = 13.1$, $E_2(H) = 38.4$, log $A_2(Cl) = 14.5$, $E_3(Cl) = 29.7$; Units for rate parameters are cm$^3$, mole, s, kcal. $\Theta_{C_4H_8} = 1500$ cm$^{-1}$, $\Theta_{C_4Cl_7} = 250$ cm$^{-1}$. Energy transfer media: air (21% O$_2$, 79% N$_2$).
SOLVENT EFFECTS ON THE THERMAL DECOMPOSITION OF 1,2-DICHLOROBENZENE

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Kent J. Voorhees
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ABSTRACT

The incineration of hazardous wastes is emerging as a positive solution to the management of hazardous organic containing wastes. To better understand the formation of products of incomplete combustion (PICs), a study of the thermal decomposition of dichlorobenzene in the presence of several organic solvents was studied. Experiments have been conducted in a laboratory scale test system using a steady state combustion environment to study the effects of co-solvents on product distribution. The introduction of chlorinated solvents resulted in an increase in the number and concentration of chlorinated compounds being formed. Conversely, the introduction of chlorophenol into the system had little effect on the product distribution. The introduction of methanol, hexane, and water into the system lowered the number of chlorinated compounds being formed.

INTRODUCTION

The incineration of hazardous organic wastes is gaining acceptance as a technique for the management of these materials. The placement of wastes containing hazardous organic chemicals in landfills represents a potential hazard to the water supplies of future generations. For this reason, landfilling of wastes is meeting with greater resistance from the public and tighter restrictions from regulating agencies.

Incineration offers a more permanent solution to handling organic compounds. During the combustion process, organic compounds are converted to carbon dioxide, water, and acid gases. A public concern to incineration is the survival of compounds from the combustion environment and the products of incomplete combustion (PICs) that are formed during the combustion reaction. This study was undertaken to define the parameters that affect the formation of PICs during combustion.

Dichlorobenzene (DCB) was selected for this study as a model of a typical industrial organic compound found in hazardous
The thermal decomposition of DCB was reported earlier. The present study expands the previous work by investigating the effect of solvents on the decomposition products from DCB.

PIC Formation in Mixtures.

Others have reported that thermal treatment of mixtures of organic compounds produce more PICs than when these compounds are treated individually. The University of Dayton Research Institute has done extensive work on the thermal stability of organic compounds. They tested a six-component mixture and found that the relative thermal stability of compounds changed when they were present in mixtures as compared to testing the individual compounds. The compounds studied were divided into two classes. One class was the compounds whose decomposition was independent of the reaction atmosphere. The other class of compounds were those species that increased in stability with decreasing oxygen concentration. From the thermal treatment of these compounds, the Dayton group identified 58 different PICs. This testing was done in different atmospheres and at different temperatures. Not all 58 compounds were present in any of the individual tests. The PICs ranged from benzene to polynuclear aromatic (PNA) compounds and from chloroform to chlorinated benzenes and naphthalenes. Many of these compounds were seen primarily from oxygen deficient conditions. It was proposed that a substantial portion of these products were formed in the initial reaction, but they are destroyed by oxidative pathways when they are available leaving only the compounds insensitive to oxidative pathways. Under oxygen deficient conditions, the competing oxidative pathways are no longer available and the PNAs show up as PICs.

Taylor and Dollinger reported on a study conducted on the thermal decomposition of chloromethane mixtures. They studied the decomposition of CCl₄, CHCl₃, CH₂Cl₂, and CH₃Cl. This group reported that the thermal stability of these compounds was dependent on the oxygen concentration and the other compounds present in the feed to the system. The evaluation of the decomposition of mixtures indicated that the degradation of CHCl₃ initiated the generation of a radical pool that lead to the decomposition of the other compounds.

EXPERIMENTAL

Test Apparatus

The test combustion apparatus has a sample introduction system, a preheater section, the high temperature reaction section, and the absorber section. The sample introduction device is composed of a pump, gas flow meters, and a spray nozzle. The pump delivers the test compounds to the introduction system at a set rate that can be adjusted to the desired level.
using a fine metering valve. The tests that added water to the system used a second pump and a spray nozzle with two tubes for delivering compounds to the system. The gas flow meters were two sets of gas proportioning valves for adjusting flows of oxygen and nitrogen to achieve the desired atmosphere for testing. The spray nozzle atomized the test compounds into the preheater section to assist evaporation of the compounds. The preheater and reaction sections were tubes packed with an aluminosilicate firebrick material. The reaction tube had a coiled tube following the packed bed section which can be adjusted in length to change the reaction time. The temperatures of the two heated zones were controlled separately. The absorber unit was a series of impingers containing methanol to condense and absorb organic compounds as they exit the heated zones.

Analysis Methods

The solvent used in the impingers for these tests was methanol. The absorbing solutions were analyzed directly using GC/MS. In addition, the solutions from the first impinger were also concentrated by extraction into methylene chloride. The methylene chloride was then evaporated to a small volume and analyzed by GC/MS for the detection of compounds present at lower concentrations.

RESULTS

The tests conducted had only two variables: the oxygen concentration and the feed mixture composition fed to the system. The oxygen concentration caused a large variation in the number and concentrations of compounds formed. The type of compounds added to the system also affected the product distribution and the concentrations of PICs. The presence of a highly chlorinated solvent in the system led to the formation of more chlorinated compounds. The presence of a non-halogenated solvent in the system tended to suppress the formation of chlorinated species.

Solvents were tested with DCB alone or in combination with other solvents. The other solvents tested were hexane, methanol, chloroform, carbon tetrachloride, chlorophenol, and water. The chlorinated solvent tests were performed to determine if their decomposition would increase the available chlorinating species and increase the number of chlorinated compounds formed. The non-halogenated solvent tests allowed determination of their effect on the chlorinating species produced by the decomposition of DCB.

The multi-solvent combinations studied were DCB/chloroform/methanol, DCB/chloroform/water, and DCB/carbon tetrachloride/water. Tests with the non-halogenated solvents mixed with the halogenated solvents were conducted to determine if the chlorination caused by the halogenated solvents could be suppressed by a hydrogen donor solvent. The results of the tests
indicated that fewer highly chlorinated compounds were formed when a hydrogen donor solvent was present.

The tests with hexane present were complicated by the low autoignition temperature of hexane. The temperature of the reaction chamber was set at 750°C, which caused auto ignition of the hexane. The flame front was observed to move back into the preheater section where it turned the last 1.5 inches of the bed bright red. This resulted in a non-controlled temperature for the tests with hexane.

The comparison of the results of DCB alone, DCB with hexane and DCB with methanol are shown in Table I. These results show a marked decrease in the amount of DCB remaining for those tests where a non-halogenated solvent was added to the system. The introduction of methanol into the feed resulted in the largest decrease in the number and concentration of chlorinated compounds formed. The test with hexane reduced the concentration of chlorobenzene, DCB, and hexachlorobenzene. It also reduced the number of compounds formed from 10 to 6. The tests with methanol reduced the concentration of DCB two orders of magnitude and reduced the number of compounds formed to 4.

Table II lists the product distribution of PICs formed for the tests of DCB, DCB/chloroform and DCB/carbon tetrachloride. The PICs were largely chlorinated compounds of various chemical classes. The chlorinated benzenes and chlorinated phenols show a general trend of increasing concentration with increasing number of chlorine atoms on the molecule. The compounds having the highest concentrations after combustion in the tests with the chlorinated solvents are the tetra- to hexachlorobenzenes. These compounds were three orders of magnitude higher in concentration than with DCB alone. The concentration of DCB remaining decreased in the tests with the chlorinated solvents, but this effect was overwhelmed by the much higher concentrations of the higher chlorinated benzenes. The tests with CCl₄ converted about 1 % of the dichlorobenzene to hexachlorobenzene. Crystals of hexachlorobenzene were also noted between the preheater and the reaction chamber indicating that some chlorination was taking place at the preheater temperatures of around 400°C.

The thermal decomposition of DCB in the presence of chlorophenol was studied to determine if this combination would lead to the formation of fused ring heterocyclic compounds. The excess oxygen test produced very few compounds and resulted in low levels of DCB or chlorophenol surviving the thermal decomposition. The compounds identified were similar to the thermal decomposition products of DCB by itself. The chlorophenol tests did follow the trends of other tests in that the decrease in the oxygen concentration produced a marked increase in the number of compounds formed and the amount of DCB remaining. The amount of chlorophenol did not necessarily follow this trend. Only small amounts of chlorophenol remained in any
of the tests. No fused ring heterocycles were formed except in the oxygen deficient test.

The studies conducted to this point had shown that increasing the chlorine content of the feed increased the number of chlorinated compounds formed. The addition of a non-halogenated solvent decreased the number of chlorinated compounds. The next investigations were designed to determine if the addition of a non-halogenated solvent to the feed could reduce the number of chlorinated compounds produced by acting as a scavenger for the chlorinating species present.

The use of methanol as a non-halogenated solvent was chosen to avoid the temperature increases caused by the ignition and burning of hexane with a flame front. To test this theory, DCB was mixed with chloroform and methanol in two different ratios. The methanol concentration was doubled in the second set of tests. Table III summarizes the results of these tests as compared to the DCB/chloroform test. The methanol showed some effectiveness at reducing the amount of chlorination with the largest reductions being in the amount of hexachlorobenzene being produced.

The addition of water into the system had a similar effect of reducing the amount of chlorination that takes place in the system. Table IV summarizes the data from the tests where water was added as a separate feed to the system. The water clearly reduced the concentrations of higher chlorinated compounds, but increased the amount of DCB that remained in the system.

CONCLUSION

The formation of products of incomplete combustion are influenced by the compounds in the combustion feed system, the temperature of the oxidizing system, and the oxygen available for combustion. The presence of highly chlorinated solvents in the feed can result in a chlorinating environment that leads to the production of more highly chlorinated PICs. The presence of non-halogenated solvents in the system produces an environment that suppresses the chlorination processes. When both types of solvents are introduced into the feed system, there is a moderate suppression of the chlorination. One possible explanation of this phenomena is that the hydrocarbon solvents produce water during combustion which acts as a hydrogen source for scavenging the chlorinating species present. Commercial scale incineration systems that use hydrocarbon fuels for maintaining combustion temperatures can actually lead to environments that suppress the formation of PICs by providing a pool of hydrogen donors to react with the released chlorine from the combustion of chlorinated compounds.
REFERENCES


### Table I
**EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C**

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<th>Compound Present</th>
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<tr>
<td>Chlorobenzene</td>
<td>18</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>372</td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>0.8</td>
</tr>
<tr>
<td>Tetrachlorobenzene</td>
<td>0.3</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>1.4</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>7.5</td>
</tr>
<tr>
<td>Additional Compounds</td>
<td>4</td>
</tr>
</tbody>
</table>

* Concentrations are in ug/gram of Mixture input.

### Table II
**EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C**

<table>
<thead>
<tr>
<th>Compound Present</th>
<th>Solvent System Additions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>None</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>18</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>372</td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>0.8</td>
</tr>
<tr>
<td>Tetrachlorobenzene</td>
<td>0.3</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>1.4</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>7.5</td>
</tr>
<tr>
<td>Chlorophenol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Dichlorophenol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Trichlorophenol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Tetrachlorophenol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Additional Compounds</td>
<td>4</td>
</tr>
</tbody>
</table>

* Concentrations are in ug/gram of Mixture input, unless noted.
### Table III
**EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C**
**Chlorinated Solvents with Methanol**

<table>
<thead>
<tr>
<th>Compound Present</th>
<th>Solvent System Additions</th>
<th>CHCl₃</th>
<th>Ratio #1</th>
<th>Ratio #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>&lt;10</td>
<td>1.42</td>
<td>1.15</td>
<td>1.19</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>40</td>
<td>850</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichlorobenzene</td>
<td>40</td>
<td>806</td>
<td>589</td>
<td></td>
</tr>
<tr>
<td>Tetrachlorobenzene</td>
<td>1.24 mg</td>
<td>869</td>
<td>748</td>
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</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>1.42 mg</td>
<td>212</td>
<td>261</td>
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<tr>
<td>Hexachlorobenzene</td>
<td>1.67 mg</td>
<td>212</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>Chlorophenol</td>
<td>&lt;0.1</td>
<td>1.2</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Dichlorophenol</td>
<td>0.7</td>
<td>8.4</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Trichlorophenol</td>
<td>0.4</td>
<td>8.9</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Tetrachlorophenol</td>
<td>6.9</td>
<td>15</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>5.3</td>
<td>5.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Additional Compounds</td>
<td>23</td>
<td>50</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

* Concentrations are in ug/gram of Mixture input, unless noted.

### Table IV
**EFFECT OF CoSolvents ON PRODUCT DISTRIBUTION AT 750°C**
**Chlorinated Solvents with Water**

<table>
<thead>
<tr>
<th>Compound Present</th>
<th>Solvent System Additions</th>
<th>None</th>
<th>CHCl₃</th>
<th>CCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>6.61 mg</td>
<td>88</td>
<td>214</td>
<td></td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>51.1 mg</td>
<td>1.76</td>
<td>5.07</td>
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<tr>
<td>Trichlorobenzene</td>
<td>334</td>
<td>1.37</td>
<td>1.11</td>
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<tr>
<td>Tetrachlorobenzene</td>
<td>0.7</td>
<td>2.49</td>
<td>3.61</td>
<td></td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>0.9</td>
<td>2.02</td>
<td>4.18</td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>2.1</td>
<td>2.44</td>
<td>4.72</td>
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<tr>
<td>Chlorophenol</td>
<td>694</td>
<td>0.4</td>
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<td>Dichlorophenol</td>
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<td>6.0</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>Trichlorophenol</td>
<td>1.2</td>
<td>4.0</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Tetrachlorophenol</td>
<td>0.9</td>
<td>6.6</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>6.3</td>
<td>3.8</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Additional Compounds</td>
<td>4</td>
<td>18</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

* Concentrations are in ug/gram of Mixture input, unless noted.
MONITORING THE EVOLUTION OF ORGANIC COMPOUNDS FROM THE THERMAL TREATMENT OF CONTAMINATED SOIL SAMPLES USING SHORT COLUMN GC/MS


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*Chemical Engineering Department, University of Utah
Salt Lake City, UT 84112

INTRODUCTION

Incineration is an effective technology for the remediation of organic chemical contaminated wastes. For solid wastes, such as contaminated soils, processes involving separate stages of a primary desorber and secondary afterburner are particularly useful. The desorption stage is currently being modeled using a particle-characterization reactor (PCR, 0-500 g capacity), a bed-characterization reactor (BCR, 0.5-5 kg), and a rotary kiln simulator (2-15 kg) to study fundamental processes such as mass transfer, heat transfer, and volatilization of contaminants [1,2]. This paper describes the analytical methods and preliminary results from monitoring the evolution of organic compounds in these and smaller reactors.

The samples are soil contaminated with a broad range of polynuclear aromatic (PNA) hydrocarbons such as those derived from coal tars. The analytical methods primarily involve mass spectrometry (MS) with a variety of sample introduction techniques. The on-going analyses include solvent and thermal extractions of soil before and after various thermal treatments as well as on-line monitoring of vapors during desorption.

EXPERIMENTAL

Samples - Contaminated and uncontaminated clay soil samples were obtained from an undisclosed site. The samples were received air dried and simply designated as "soil A" and "soil B". The soils were analyzed for approximate mineral content by Fourier Transform Infrared (FTIR) spectroscopy of standard KBr pellets. Extracts were prepared from mg to g size samples by ultrasonification with repetitive aliquots of methylene chloride (CH2Cl2). Further, standard solutions of PNA's from naphthalene through dibenzoanthracenes were prepared for calibration purposes at 1, 23 ng/ul and 200 ng/ul in methylene chloride.

Extract Gas Chromatography/Mass Spectrometry (GC/MS) - GC/MS analyses of the extracts (procedure described above) were performed using a Hewlett-Packard 5890 chromatograph with a 15 m x 0.25 mm i.d. x 0.25 µm film thickness DB-5 column (J&W Scientific). Extracts were injected either by split injection or by flash vaporization in a Curie-point pyrolysis GC inlet [3] using 350 C Curie-point wires in an inlet set at 250 C. For the Curie-point injection, 2 to 10 ul of CH2Cl2 extract were concentrated on the pyrolysis wire with only limited loss of the smaller PNA's. The column was temperature programmed from 40 to 300 C at 15 C/min. An Ion Trap Detector (ITD, Finnigan MAT) was scanned from m/z 50 to 350 at 2 scans/sec.

Solids Probe MS - Soil samples were analyzed directly by use of a solids probe on a Ion Trap Mass Spectrometer (ITMS, Finnigan MAT). 1-3 mg samples were
placed in aluminum vials with 0.1 mm diameter holes in the press fit caps. The probe tip was then heated from 40 to 500 °C at 60 °C/min to desorb the organics directly into the ion trap maintained at 120 °C. The mass spectrometer was scanned from m/z 50 to 350 at 2 scans/sec. PNA standards were deposited from CHCl₃ solutions into the vials with and without soil substrate. Both uncontaminated and previously desorbed soils were used as substrates for the standards in separate experiments.

On Line Short Column GC/MS - The desorbing organic vapors were monitored during thermal treatment using a newly designed vapor sampling inlet with short column GC on a miniaturized ITMS (MINITMASS) all of which is described in detail elsewhere [4,5,6]. The system used a 1 m x 0.18 mm i.d. x 0.4 μm film thickness DB-5 column (J&W Scientific) in the standard ITD transfer line for isothermal operation. For these analyses the MINITMASS was operated in electron ionization mode with software features for enhanced sensitivity [6,7]. Retention time standards for various PNA’s were acquired by direct injection of micro liter volumes of PNA standard solutions. Various inlet and column temperatures were used.

Thermal Treatment Reactors - Preliminary micro scale heat treatments (5-60 mg) were performed by thermogravimetry (TG) (Perkin Elmer TGA 7). In initial vapor sampling tests, 1 μg each of naphthalene and acenaphthylene were added to 10 mg of clean soil and then heated at 50 °C/min to 600 °C while the 125 or 200 °C vapor inlet sampled the TG furnace outlet at 30 s intervals. In other tests, 50-60 mg portions of soil A were heated at 100 °C/min to 250, 350 or 450 °C, held for 5 min and then cooled at 50 °C/min under He. The thermal treated soils were then analyzed by the extraction GC/MS and solids probe MS techniques.

The laboratory-scale reactors for particle and bed characterization, and the rotary-klin simulator are described in detail elsewhere [1,2]. At the time of this writing, vapor sampling of test soils A and B was not completed. However, these results will be included in the oral presentation. A set of preliminary experiments in the bed-characterization reactor (BCR) have been conducted where “clean” clay soils were loaded with 0.5 % of either toluene, ethylbenzene, isopropyl benzene, or t-butylbenzene. In these runs, the tray of organic-loaded soil was placed beneath radiant heaters directly in the 536 °C preheated air stream. The evolved gases were sampled at 60 s intervals for repetitive short column GC/MS analysis. The vapor inlet was operated at 160-175 °C and the transfer line at 30 °C isothermal.

RESULTS AND DISCUSSION

Extract GC/MS - Figure 1 shows a series of ion chromatograms from the flash vaporization GC/MS of the soil A extract. The total ion chromatogram is shown for the complete run (Figure 1a) and as an expanded short segment (Figure 1b). Single ion chromatograms are shown for m/z 228 (Figure 1c), 252 (Figure 1d) and 276 (Figure 1e). This data demonstrates the complexity of the chemical contaminants and the wealth of detailed qualitative and quantitative data that are available through this technique using a high resolution capillary column of normal length. Note that 5 or more isomers of benzofluoranthenes and benzopyrenes are distinguishable in the trace of m/z 252. The concentrations of compounds smaller than phenanthrene are underestimated in this chromatogram due to premature evaporation from the Curie-point wire.

Solids Probe MS - Figure 2 shows the solids probe MS analysis of soil A. The single ion chromatograms indicate that the PNA’s were desorbed from the soil.
into the MS high vacuum over a broad temperature range of 100 to 400 C when heated at 60 C/min. These ion traces suggest the strong interaction of the PNA's with the clay soil surface since these same compounds completely evaporate from a sample vial without the soil at temperatures less than 200 C. Note that there is no separation of the various isomers as was seen with the chromatography in Figure 1.

Vapor Sampling GC/MS - Figure 3 is a set of ion chromatograms from the vapor inlet short column GC/MS analysis of PNA standard solution. This figure illustrates how compounds eluting in the 9 min to 18 min portion of the chromatogram shown in Figure 1 are compressed into a 1 min analysis on the isothermal short column at 250 C. Although the chromatographic resolution is greatly reduced from that of Figure 1, there is still a clear separation of the benzofluoranthenes from the benzopyrenes as seen in the m/z 252 trace. The significant advantage is that the partial GC/MS analysis can be repeated each 60 sec versus the 20 min in Figure 1 and this analysis still gives some isomer information beyond that which can be obtained in direct MS methods such as seen in Figure 2.

Thermal Treatment Analyses - Figure 4 illustrates the monitoring of PNA evolution from thermal treatment of the soil using the short column GC/MS system on-line. In this analysis, the 4 min to 7 min portion of the chromatogram in Figure 1 has been compressed into a 30 sec segment of Figure 3. For this preliminary test, naphthalene and acenaphthylene were repetitively analyzed each 30 sec as they were evolved from 10 mg of soil in a thermogravimetry (TG) crucible. Note that the profiles of consecutive naphthalene (m/z 128) and acenaphthylene (m/z 152) peaks trace the evolution of these compounds from the soil at the TG temperatures indicated. The naphthalene is desorbed from the soil at higher temperatures than the higher boiling acenaphthylene possibly due to the fact that it was the first one coated on the soil and thus had first access to the strongest adsorption sites. Although equal amounts of each compound were placed on the soil, recondensing of the acenaphthylene in cold regions of the TG oven greatly attenuated its signal.

Samples of soil A were heated in the TG to 250, 350, or 450 C (without on-line vapor analysis) and then analyzed by extraction GC/MS and solids probe MS. Preliminary analysis of these data indicate that there were virtually no PNA's left on the soil heated to 450 C in helium. The solids probe MS data on selected PNA's in the original soil and the 250 and 350 C thermal treated soils are listed in Table 1. Although these data show the expected reduction of these compounds from the heated soils, the actual solids probe ion profiles indicate that the remaining amounts are more tightly bound than the major portions of the original contamination. This result is readily explained if one simply assumes that the first monolayer of PNA's on the clay surface is more strongly adsorbed than additional layers. Further, a layer of black char began to form at 350 C (in helium), which might be a secondary binding site. At present it is unclear to what extent this char was formed from the PNA contaminants versus native soil humic substances.

Evolution profiles of selected compounds from .5 wt % toluene loading on a clay soil are presented in Figure 5. 600 g of soil was heated to 536 C in the BCR. Three secondary products are shown at concentrations of 1 ppb to 1 ppm (in air). In addition to the reaction products shown in the figure, the following were also detected at similar concentrations: benzyl alcohol, bromotoluene, bromobenzene, quinone, benzonitrile, xylene, ethylbenzene, chlorotoluene, and dichlorobenzene. The benzaldehyde and benzylalcohol are expected as partial oxidation products. The exact sources of the other compounds are as yet not clear.
uncertain although it can be stated that these were not impurities in the original solvent and there was approximately 15 ppm chlorine found in the original soil. The quantity and diversity of these products gives some idea of possible secondary reactions and desorption characteristics expected with the PNA's.

CONCLUSIONS

These preliminary results clearly demonstrate the potential of mass spectral techniques for studying the effectiveness of thermal treatment in contaminated soil remediation. Solvent extraction followed by high resolution GC/MS is the method of choice for detailed examination of soils before and after treatment. Solids probe MS is a rapid technique for screening soils and can offer additional information on how the contaminant is bound to the soil. The vapor sampling short column GC/MS system is a powerful tool for on-line monitoring of the desorbed gas phase products which are important to identify for desorber optimization and afterburner design. Isothermal operation of the short column is a major limitation to the boiling point range of compounds which can currently be analyzed on a rapid repetitive basis and plans are underway for making it temperature programmable.

ACKNOWLEDGEMENTS

This work was funded by the Gas Research Institute, David Linz, Project Manager, and the Advanced Combustion Engineering Research Center (ACERC). Funds for the ACERC Center are received from the National Science Foundation, the State of Utah, 22 industrial participants and the U.S. Department of Energy. The technical assistance of Robert Lo is also appreciated.

REFERENCES

### TABLE 1
Approximate Concentrations in ng/mg (ppn) of Selected PNA's on "As Received" and TG Thermally Treated Soil A

<table>
<thead>
<tr>
<th>Compound m.w.</th>
<th>Soil A</th>
<th>250 C</th>
<th>350 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>600</td>
<td>66</td>
<td>19</td>
</tr>
<tr>
<td>202</td>
<td>200</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>278</td>
<td>16</td>
<td>14</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1. GC/MS ion chromatograms from the analysis of the soil A extract on a 15 m column.
Figure 2. Solids probe MS ion chromatograms from the thermal desorption of soil A directly into the mass spectrometer high vacuum.

Figure 3. Selected ion chromatograms from the vapor sampling GC/MS analysis of a PNA standard solution.
Figure 4. Ion chromatograms for repetitive on-line sampling using vapor inlet short column GC/MS during a TG soil desorption.

Figure 5. Peak area profiles for 3 selected reaction products produced from toluene desorption.
NEWSPAPERS - A MAJOR CONTRIBUTOR TO THE MUNICIPAL SOLID WASTE STREAM

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Each year Americans must deal with over 160 million tons of municipal solid waste. This material (the stuff we throw away with very little concern as to where it goes) is a pollutant in itself and no matter how well managed, will have some measure of environmental impact. Integrated solid waste management techniques reduce the adverse impact and minimize the risk that may be incurred by relying on only one disposal alternative.

In order to manage heterogeneous garbage in a safe and sane manner, local governments must use all solid waste management options available. They include: waste reduction (volume or toxicity); recycling or reuse; treatment for volume reduction, organic destruction, and recovery of energy; and land disposal. While each option can be used to manage a different materials in the municipal waste stream, none can do the job alone. All have the potential for causing environmental harm and must be performed carefully to minimize the adverse impact. For example, reducing the volume of food packaging could increase the potential for bacterial and viral exposure; recycling uses energy and releases waste products into the environment that could contaminate ground and surface waters and contribute to regional air pollution; waste-to-energy plants must control air emissions to safe levels and ensure proper management of ash so as not to endanger water supplies.

Landfills, which have the greatest potential for contamination, must control disease vectors, air emissions (fugitive dust and organic vapors) and leachates generated during the decomposition of the waste.

Ogden Projects, Inc., (OPI) is involved with integrating all solid waste management options. Although the company’s primary focus is designing, building, and operating waste-to-energy facilities, it also operates landfills and manages recycling programs. Since the most important aspect of municipal solid waste (MSW) management is public health protection, non-management of waste is as much a cause for concern as the AIDS epidemic. If MSW is not collected or just dumped at the edge of town, there will be health incidents arising from the bacteria and virus contained in the trash that is spread by wind, rain, and rodents. While integrated solid waste management will mitigate these kinds of adverse health incidents, no one method will eliminate all potential problems.
One of the most controversial problems with MSW management is the trace toxic constituents of everyday, short-lived, consumer products. From a management perspective, decreasing the large volume of material is a priority. However, from the perspective of long-term environmental impact, toxicity is much more important.

Keeping this in mind, OPI studied the potential impact of newspapers, an item that is discarded daily. Newspapers represent the single largest item in the daily waste stream, accounting for 10-20 percent of municipal waste. In New York City, newspapers account for 15 percent of all municipal solid waste. One daily newspaper admitted that it was responsible for 20 percent of municipal waste generated on Long Island.

Newspapers are the most readily recycled commodity in municipal solid waste. They have the potential to release about 8,000 British Thermal Units (BTUs) per pound if burned in a waste-to-energy facility. Unfortunately, when placed in a landfill, they biodegrade very slowly, producing organic acids that have the potential of carrying toxic constituents to water supplies. By performing a simple chemical analysis, it is evident that the amount and the type of toxics released into the environment from this short-lived product is alarming.

OPI chose a major metropolitan newspaper with one of the 10 largest circulations in the United States. In January 1988, newspapers were purchased at a convenience store for a one-week period and sent to two separate laboratories for chemical analysis. The daily newspapers were shredded, composited, and subjected to a series of organic and inorganic analyses. Likewise, the Sunday edition was treated and processed and, additionally, a second Sunday edition was analyzed for dioxin. Versar, Inc., of Columbia, Maryland (metals, organics, EP Tox, etc.), and Triangle Labs, Research Triangle Park, North Carolina (dioxin, furan), participated in the analyses.

The newspaper reported that it used eight percent recycled "fiber". Although it was assumed that each roll of newsprint contains eight percent recycled fiber, this could also be taken to mean the eight percent of the time the paper is printed on recycled newsprint. The chemical analysis showed that the newspaper contained a number of toxic, carcinogenic, mutagenic and teratogenic elements and chemical compounds. While the presence of these trace constituents is low, the amount of toxics flowing into the ecosystem is noteworthy.

Circulation data is as follows:
DAILIES SUNDAY

<table>
<thead>
<tr>
<th></th>
<th>Daily</th>
<th>Sunday</th>
<th>Daily</th>
<th>Sunday</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circulation</td>
<td>641,000</td>
<td>682,000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight</td>
<td>5.87 lbs.</td>
<td>3.16 lbs.*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tons/Year</td>
<td>97,829.42</td>
<td>56,033.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* A Sunday issue published in December 1987 weighed 4.98 lbs. That equates to 88,174.88 tons of Sunday issues per year. This number, however, is somewhat high given the extraordinary amount of advertising in holiday editions.

The following generation rates (rounded to the nearest 1,000) were used to calculate the flow into the ecosystem annually: 100,000 tons/year for dailies; 70,000 tons/year for Sunday; 170,000 tons/year total.

Organics

The trace organic compounds found in the newspapers are listed in the following table. The majority (5) of these compounds are solvents and are most likely associated with the inks as vehicles and/or press cleaners. Hexachlorocyclohexane is a pesticide and is probably a residual from the papermaking process. The phenol is also a probable residual. The data is quantified in parts per billion and pounds per year.

<table>
<thead>
<tr>
<th>Organics</th>
<th>Daily</th>
<th>Sunday</th>
<th>Daily</th>
<th>Sunday</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Chloride</td>
<td>94</td>
<td>69</td>
<td>18.8</td>
<td>9.66</td>
<td>28.46</td>
</tr>
<tr>
<td>Acetone</td>
<td>230</td>
<td>630</td>
<td>46</td>
<td>88.2</td>
<td>134.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>130</td>
<td>1800</td>
<td>26</td>
<td>252</td>
<td>278</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>22</td>
<td>480</td>
<td>4.4</td>
<td>67.2</td>
<td>71.4</td>
</tr>
<tr>
<td>Xylenes</td>
<td>130</td>
<td>2300</td>
<td>26</td>
<td>322</td>
<td>348</td>
</tr>
<tr>
<td>Hexachlorocyclohexane</td>
<td>23</td>
<td>23</td>
<td>4.6</td>
<td>3.22</td>
<td>7.82</td>
</tr>
<tr>
<td>Phenols</td>
<td>1100</td>
<td>1000</td>
<td>220</td>
<td>140</td>
<td>360</td>
</tr>
</tbody>
</table>

* PPB. All other - pounds per year.

Dioxins

Because of the high cost of analysis, only one dioxin/furan analysis was performed on the Sunday edition. The analysis showed the presence of dioxin/furan at the same levels, and with the same isomer profile, as many other paper products analyzed. Therefore, it was assumed that the dailies also contained the same levels. The dioxin/furan releases to the ecosystem are based on the 170,000 tons/year figure.

Interestingly, paper contains the most toxic isomers of
dioxin/furan in the highest concentrations. In comparison, ash and air emissions from resource recovery facilities have low relative concentrations of the most toxic isomers.

The total concentration of dioxin/furan in the newspaper was 248.49 parts per trillion (ppt). Converted to a 2,3,7,8 TCDD toxic equivalent basis (US EPA method), the amount is 11.158 ppt. This results in more than a gram (.004 lbs) of 2,3,7,8 TCDD equivalents entering the ecosystem each year. By comparison, Ogden Martin's Marion County facility, which burns an equivalent tonnage of waste each year (170,000), emits 20 times less dioxin/furan to the environment.

**PCDD/PCDF ANALYSIS**

Concentration and Toxic Equivalents (EPA Method) (ppt)

<table>
<thead>
<tr>
<th>NAME</th>
<th>CONCENTRATION</th>
<th>MULTIPLIER</th>
<th>TOXIC EQUIVALENT</th>
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<tbody>
<tr>
<td>2378-TCDD</td>
<td>3.915</td>
<td>1.0</td>
<td>3.915</td>
</tr>
<tr>
<td>Other-TCDD</td>
<td>ND</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>2378-Sub-HxCDD</td>
<td>ND</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>Other-HxCDD</td>
<td>2.181</td>
<td>0.0004</td>
<td>0.00087</td>
</tr>
<tr>
<td>1234678-HpCDD</td>
<td>12.841</td>
<td>0.001</td>
<td>0.0128</td>
</tr>
<tr>
<td>Other-HpCDD</td>
<td>25.747</td>
<td>0.000001</td>
<td>0.000257</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>69.504</td>
<td>0.1</td>
<td>6.95</td>
</tr>
<tr>
<td>Other-TCDF</td>
<td>131.381</td>
<td>0.001</td>
<td>0.131</td>
</tr>
<tr>
<td>23478-PCDF</td>
<td>1.472</td>
<td>0.1</td>
<td>0.147</td>
</tr>
<tr>
<td>Other-PCDF</td>
<td>1.449</td>
<td>0.001</td>
<td>0.00145</td>
</tr>
<tr>
<td>ppt</td>
<td>248.49</td>
<td></td>
<td>11.158</td>
</tr>
</tbody>
</table>

Heavy metals

Two types of heavy metals analyses were conducted. The EP Toxicity test, which was the first, is a leaching test that attempts to simulate what occurs in a landfill. It indicated the newspaper did not exhibit hazardous waste characteristics and metals did not leach out at levels above the regulatory threshold. There are, nevertheless, heavy metals present in the newspaper that were detected as a result of a chemical analysis procedure. The following table lists the metals detected in parts per million and in pounds/year to the ecosystem.
**HEAVY METALS**

<table>
<thead>
<tr>
<th></th>
<th>DAILY*</th>
<th>SUNDAY*</th>
<th>DAILY</th>
<th>SUNDAY</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>14.0</td>
<td>17.0</td>
<td>2800</td>
<td>2380</td>
<td>5180</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.021</td>
<td>0.1</td>
<td>4.2</td>
<td>14</td>
<td>18.2</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.68</td>
<td>0.94</td>
<td>136</td>
<td>131.6</td>
<td>267.6</td>
</tr>
<tr>
<td>Copper</td>
<td>4.9</td>
<td>13.0</td>
<td>980</td>
<td>1820</td>
<td>2800</td>
</tr>
<tr>
<td>Iron</td>
<td>7.10</td>
<td>44.0</td>
<td>1420</td>
<td>6160</td>
<td>7580</td>
</tr>
<tr>
<td>Lead</td>
<td>0.43</td>
<td>1.8</td>
<td>86</td>
<td>252</td>
<td>338</td>
</tr>
<tr>
<td>Manganese</td>
<td>38.0</td>
<td>50.0</td>
<td>7600</td>
<td>7000</td>
<td>14,600</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.0014</td>
<td>0.0066</td>
<td>0.28</td>
<td>0.924</td>
<td>1.204</td>
</tr>
<tr>
<td>Silver</td>
<td>0.032</td>
<td>0.14</td>
<td>6.4</td>
<td>19.6</td>
<td>26</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.8</td>
<td>11.0</td>
<td>560</td>
<td>1540</td>
<td>2100</td>
</tr>
</tbody>
</table>

* PPM  All other - pounds per year.

Newspaper disposal results in seventeen plus tons of heavy metals, for which primary and secondary drinking water standards have been established, being released into the environment each year. In comparison, Ogden Martin’s Bristol, Connecticut, facility, which burns an equivalent amount of trash each year, emits only one sixth as much lead.

**Additional Impacts**

If all of these newspapers were placed in landfills, there would be the potential for generating 699,125 (350 tons) of toxic hydrogen sulfide gas from the biological decomposition of the sulfur contained in the paper each year. On the other hand, if all were burned, 658 tons of sulfur dioxide, 105 tons of hydrogen chloride gas, and 127.5 tons of nitrogen oxide would be produced.

Newspaper (newsprint) is a readily recycled material. When recycled, the organic solvents and metals in the inks become waste. This particular newspaper prints their product on ninety-two percent virgin stock and eight percent recycled paper stock. During the recycling operation, in order to produce 13,600 tons of recycled newsprint, at least 1,360 tons of waste are generated. This waste consists of short unusable fibers and ink.

If any paper other than newsprint is used to produce recycled news, additional waste in the form of fillers and coatings is generated. All of this waste is contained in the pulping liquids and removed as a sludge in a complex wastewater treatment system. This sludge is often managed as a RCRA hazardous waste under Subtitle C of the Resource Conservation and Recovery Act.

Most volatile organics contained in the incoming paper flow into the receiving body of water. While the levels of organic compounds and metals detected in the newspaper do not represent an imminent threat to public health, their presence is of concern.
Because all of these compounds contribute to the environmental loading of toxic compounds, the toxicity of newspapers should be reduced. There are less toxic inks, vehicles, and solvents available for substitution.

The American Newspaper Publishers Association (ANPA), which represents approximately 1,400 daily and weekly newspapers in the US and Canada, established a set of voluntary standards for inks containing no lead, chromium, or cadmium.

ANPA has also developed standards for black ink, which has very low levels of aromatic hydrocarbons, and uses only carbon black as the pigment. In addition, ANPA has developed a water-based ink printing process. Approximately 40 newspapers have started using this new low environmental impact process. Although ANPA's efforts represent a significant first step, they are non-enforceable and address the newspaper printing process only, and not the "slick" advertising and weekend supplement inserts.

Heavy-metal based pigments are often used to produce these "slick" supplements as well as the colored ads that appear on newsprint. This fact raises questions regarding newspaper advertising. Given our free enterprise system, it is highly unlikely that newspaper publishers would eliminate advertising. If such a revolutionary idea were implemented, it would result in a weight reduction of as much as ninety-five percent, and a significant reduction to the flow of toxic compounds into the environment.

Because a newspaper is dependent on advertising revenue to continue publication and maintain high circulation, eliminating advertising in Sunday or daily editions is not highly likely in the near future.

Although it is unrealistic to expect newspapers to totally eliminate advertising, they could contribute to solving America's solid waste crisis by taking steps to reduce the toxicity of their product, and exercising discretion with respect to "slick" advertising supplements.
MUNICIPAL WASTE COMBUSTION ASH: TESTING METHODS, CONSTITUENTS AND POTENTIAL USES

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Alexandria, VA 22304
(703)751-2523

INTRODUCTION

This paper focuses on the content of combined ash, which represents the non-combustible portion of municipal solid waste. The term "ash" refers to all the solid residue streams of a municipal solid waste combustion system. This included: the bottom ash (approximately 85 to 95 percent of the total), also referred to as "clinker"; ash that collects on boiler, superheater and economizer tubes often referred to as "soot"; ash that is removed from the flue gas via the boiler passes, and the fly ash collected by the air pollution control equipment. The last type of ash is a combination of the solid material, as well as the reacted and unspent reagent from the acid gas scrubbers, that is collected after reaction in the scrubbers by the particulate collection equipment (e.g., the fabric filter or electrostatic precipitator). Bottom ash mainly comprises bottles, cans, auto parts, broken appliances and a myriad of other things that do not lend themselves to complete combustion. Fly ash originates from the ever-present fraction of inorganic compounds in paper, wood, plastic, rubber and food wastes. For example, there are clays in papers, stabilizers in plastics, pigments in printing, inks and mineral salts in vegetables and other products. In other words, the constituents that comprise the two types of ash represent the unavoidable, inorganic, by-products of everything that is thrown away.

By volume, the ash is approximately one-tenth to one-twentieth of the original incoming municipal solid waste. By weight, it represents approximately one-fourth of the original amount. It is much denser than raw solid waste and takes up much less space for ultimate disposal.

ENVIRONMENTAL BENEFITS OF COMBUSTING SOLID WASTE

Volume reduction, converting large amounts of solid waste material into smaller volumes, is a basic environmental protection practice that has been used for thousands of years. Many federal solid waste regulations are based on this premise and it has been a preferred solid waste management option for more than a century. Unfortunately, despite successful reduction and recycling programs, the United States will still need to combust the remainder of the waste stream.

Combusting municipal solid waste and converting it into energy has three basic purposes. First and foremost, the high temperatures accomplish sterilization and deny food and habitat
to disease vectors such as rats and flies. Secondly, volume reduction is successfully accomplished. And, thirdly, useful energy is captured. Throughout history, municipal solid waste was combusted to control disease and reduce volume. Up until the 1960s, open dumps were often set afire as a method of disease (vector) control and to make room for more garbage. Adverse repercussions such as brush fires, rat migration, air pollution, and worker fatalities led to public health problems that made open burning unsafe. However, burning municipal solid waste in a carefully-controlled furnace and managing ash efficiently can satisfy the original objectives without causing environmental harm. While volume reduction to reduce the burden of final waste disposal is essential, combustion can also convert municipal solid waste into energy that can be recovered.

The conversion of raw, unprocessed municipal solid waste into a smaller volume of ash results in long-term land preservation because ash disposal requires less space. There are many differences between disposing of raw municipal solid waste and landfilling ash.

Many environmental problems associated with municipal solid waste disposal can be reduced, mitigated, or eliminated with combustion. Landfilling of raw municipal solid waste generates odors, methane gas, and many other toxic and reactive gases. All these gases originate from the biological decomposition of organic matter. While odors are more annoying than dangerous, methane gas migration from poorly-designed and/or operated landfills has caused explosions in structures located nearby, resulting in millions of dollars of property damage and loss of life. Waste-to-energy ash is biologically inactive, generating no odors or explosive, toxic, or reactive gases from the landfill.

Potential groundwater contamination can occur from any material disposed of in a landfill. This contamination is the result of moisture contained in the material, or rain, or surface water, infiltrating the material and leaching out toxic contaminants. Because organics predominate raw municipal waste, leachate from a landfill is also highly organic. In addition, it is acidic because of the biological activity within the landfill. The organic acids have a much greater potential to carry toxic compounds and elements into groundwater than the leachate from an ash landfill. In contrast, ash leachate that forms in small amounts (since infiltration through dense ash is very slight) contains only inorganic compounds -- salts and metals -- that do not easily travel through soil. By locating the landfill in the proper hydrogeological setting and/or by using liners and leachate collection systems, both leachates can be prevented from entering groundwater. Because ash leachate is predominantly inorganic, it can be contained with a simple lining system, and is not difficult to treat. Subsequently, the potential for groundwater contamination is much less than from a raw municipal solid waste landfill.

This has already been demonstrated in other parts of the world: Wurzburg, Germany; Marion County, Oregon; Denmark and
Sweden. In addition, the United States Environmental Protection Agency (EPA) is investigating ash leachate in a joint study with Marion County at the county’s Woodburn monofill.

Dust represents another problem at landfills that can be reduced with combustion. Municipal solid waste is a very dusty material. When it is deposited in a landfill, without adequate controls, bits and pieces blow around. The compaction process requires driving large bulldozer-type vehicles over the municipal solid waste until it is compacted, which may increase dust generation. On the other hand, the semi-wet ash is delivered to the landfill and does not result in any fugitive dust. Since wet ash is so dense, it does no require much compaction. Consequently, very little airborne material is released into the environment during ash disposal.

Unlike ash residue, raw waste undergoes biological decomposition during the many years it remains placed in the landfill, volume reduction occurs gradually over time; it is an ongoing, slowly-evolving process. This continuous shrinkage causes the surface of the landfill to subside and requires extensive reworking of the soil. The subsidence also results in increased infiltration of rain water, which in turn produces more leachate. An ash landfill, however, becomes a stable mass within days of initial placement and requires only simple maintenance of the final cover. No subsidence whatever occurs. Modern waste-to-energy facilities reduce the volume of material and mitigate the potential public health problems associated with the ongoing land disposal of municipal solid waste.

**PHYSICAL AND CHEMICAL PROPERTIES OF ASH**

Unprocessed municipal solid waste contains varying percentages of inert materials that eventually become the ash or solid residues upon combustion in a resource recovery facility.

The volume reduction achieved by combustion increases the concentration of the metals in the ash versus the unburned municipal solid waste. The total amount of metals, however, have not increased. The increase in concentration cannot be any higher than the weight reduction (that is a 4-to-1 weight reduction of waste to ash, or 80 percent, increases concentration by a factor of five). Regardless of whether it is municipal solid waste that is landfilled, or ash from a resource recovery facility, the total amount of metals going in will remain the same. No data is available to suggest that the combustion process changes the properties of the metals to make them any more dangerous. On the contrary, leachate data from raw solid waste landfills suggests higher metal mobility because of biological activity and the presence of organic acids. From the available data on ash collected by Ogden Martin, the following list shows average metal concentrations in categories of major, minor and trace constituents:
### METALLIC ASH CONSTITUENTS

<table>
<thead>
<tr>
<th>Major</th>
<th>%</th>
<th>Minor</th>
<th>%</th>
<th>Trace</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>3</td>
<td>Copper</td>
<td>0.1</td>
<td>Arsenic</td>
<td>0.003</td>
</tr>
<tr>
<td>Calcium</td>
<td>8</td>
<td>Lead</td>
<td>0.2</td>
<td>Barium</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron</td>
<td>10</td>
<td>Manganese</td>
<td>0.6</td>
<td>Cadmium</td>
<td>0.003</td>
</tr>
<tr>
<td>Sodium</td>
<td>6</td>
<td>Molybdenum</td>
<td>0.1</td>
<td>Chromium</td>
<td>0.02</td>
</tr>
<tr>
<td>Silica</td>
<td>30</td>
<td>Potassium</td>
<td>0.4</td>
<td>Mercury</td>
<td>0.0006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Titanium</td>
<td>0.7</td>
<td>Selenium</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zinc</td>
<td>0.3</td>
<td>Silver</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

In addition to the metals listed above, ash contains many other elemental compounds that make up the bulk of the material. Oxygen, sulfur, chlorine, which occur as oxides and sulfates, and chlorides account for more than 30 percent of the ash. There are also trace elements that can be detected at the lowest detection levels of modern analytical chemistry. This is also true of organic compounds, other than unburned or fixed carbon.

Based on an average of available data, the physical properties of ash can be tabulated as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>one or two tons per cubic yard</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>approximately one to three</td>
</tr>
<tr>
<td>Moisture</td>
<td>15% to 25%</td>
</tr>
<tr>
<td>Grain Size</td>
<td>10% similar to clay</td>
</tr>
<tr>
<td></td>
<td>40% similar to sand</td>
</tr>
<tr>
<td></td>
<td>30% similar to gravel</td>
</tr>
<tr>
<td></td>
<td>20% larger than gravel</td>
</tr>
<tr>
<td>Permeability</td>
<td>$10^{-3}$ to $10^{-4}$ cm/sec as landfilled</td>
</tr>
<tr>
<td>Texture</td>
<td>Wet concrete-like or wet sand and gravel-like</td>
</tr>
</tbody>
</table>

### ASH MANAGEMENT AT AN OPERATING FACILITY

The Martin GmbH mass-burn design encompasses the closed-system concept to handle the process residue streams so that no employees, visitors or nearby residents will be exposed to airborne dust. All hoppers from the boiler to the air pollution control device have sealed, air-locked valves that transfer the fly ashes and/or dry scrubber reagent and reaction products to sealed screw or drag conveyors. In turn, these conveyors deliver all of the combined fly/bottom ash stream to the sealed discharger at the lower end of the furnace; just below the level where the bottom ash drops off the stoker grate.

As the bottom ash falls down the ash discharger chute into the quench water bath, the fly ash is captured, moistened and combined with the bottom ash before it is hydraulically discharged by a ram. The ram extrudes and dewater the ash prior to dropping it on the conveyor system. At this point, the ash has the consistency of wet concrete.

As it moves outside the boiler building, an enclosed conveyor transfers it to the ash storage building or another area to await transfer to covered, water-tight trucks or containers for eventual utilization or landfill burial. At any point, where the
employees or the public may be exposed, the ash system is either sealed or the ash moistened and enclosed in a building or conveyor.

ASH CHARACTERIZATION

Since the state environmental regulatory agencies have difficulty accurately predicting the potential adverse effects of burying waste, these governmental agencies typically have a two-pronged approach to the problem. Specific types of wastes, with high potential for causing environmental harm, are listed as "hazardous".

Secondly, regarding other wastes including ash, these agencies have established four broad characteristics to use in identifying waste that must be managed as "hazardous waste". The characteristics include ignitability, corrosivity, reactivity, and extraction procedure toxicity. This last characteristic is often applied to municipal waste combustion ash. The EP toxicity characteristic is determined by a devised laboratory test that attempts to mimic the landfill environment and disposal scenario of five percent unknown waste and 95 percent raw municipal waste in an unlined landfill.

Many problems occur with tests that take a small sample of waste, subject it to a laboratory analysis and then use the results to predict how larger quantities of hypothetical waste will really behave. For example:

- How do you obtain representative samples?
- How do you prepare these samples for laboratory analysis?
- What type of test is most appropriate for the manner in which the waste will be managed?
- How should varying results be interpreted?

Researchers in the waste management field have proposed additional tests that may be more appropriate. Currently, however, the ultimate test is one of sampling the actual leachate/groundwater from the managed (or mismanaged) land disposal unit.

The EP Toxicity test is the current test method employed by the EPA to determine if an unknown waste that may be subject to leaching in a landfill should be managed as a "hazardous waste". The Toxic Characteristics Leaching Procedure (TCLP) and other tests have also been proposed (published in the Federal Register and implemented for certain regulations as the land ban for certain hazardous wastes). Indeed, after much consideration, some agencies have eliminated or exempted waste-to-energy ash from laboratory testing.

Before considering what test should be used for regulatory or research purposes, a method must be available to obtain a representative sample. One cannot obtain an accurate sample by simply "grabbing" a small portion of the ash residue from a resource recovery facility, test it and declare that it is "hazardous". There is a very deliberate and detailed sampling procedure mandated by Section 1 of SW-846 (Test Methods for
Evaluating Solid Waste: Physical/Chemical Methods, U.S. EPA, Publication #SW 846, July 1982 as amended. Only by following these guidelines can one attempt to obtain representative ash samples and conclude within a certain degree of confidence, that the ash does or does not exhibit the characteristic of EP Toxicity, that it is hazardous by the TCLP, or by any other leaching procedure.

Even when Section 1 is closely followed and an extensive sampling program is performed, it may not necessarily provide representative samples. To adequately state the results within a 90 percent confidence limit, the number of samples cannot be determined until all the results of the samples are analyzed statistically. After following the sampling guidelines in SW-846, a difficult task of sample preparation must be applied.

The preparation methods in SW-846 result in the collection of many samples each weighing 50 to 100 pounds. These must be reduced in size to pass through a nine millimeter sieve. Typically, this step has been omitted in most ash sampling programs. The samples are usually screened and the subset of the sample, which passes through the nine millimeter screen, is the portion subjected to laboratory analysis. This, however, results in an unrepresentative sample in violation of the procedures in SW-846. Furthermore, some laboratories have failed to maintain the sample's moisture content or have completely dried the samples to ease preparation.

Once a representative sample is obtained, there are many laboratory tests that can be performed to collect data about it. This data is then used to determine leaching characteristics. Different official procedures require different tests for various characteristics that the ash exhibits. These tests include:

1. Percent Moisture
2. Particle Size and Structural Integrity
3. pH
4. Selected Anions (negatively-charged ions) and Cations (positively-charged ions)
5. Total Metals
6. Organic and Carbonaceous Material
7. Leaching or Extraction Tests, such as the EP Toxicity Test, the TCLP Test, a De-Ionized Water Leaching Test, a Solid Waste Leaching Procedure Test or Column or Lysimeter Tests

The extraction fluids are analyzed by atomic absorption or inductively-coupled argon plasma (ICAP). The analytical data are then examined for quality assurance/quality control and treated statistically to determine the results and confidence limits.

As rigorously as possible, OMS has followed the procedures in Volume 40 C.P.R. 261.24 and SW-846 in sampling and analyzing the ash from its operating facilities located in: Tulsa, Oklahoma; Marion County, Oregon; Hillsborough County, Florida; Bristol, Connecticut and Alexandria, Virginia. The ash did not exhibit the characteristic of hazardous waste in any instance.
The TCLP which is under development appears to be more consistent in yielding results. Sample collection and preparation problems are the same as with the EP (grinding portions of the ash that will not break down in the landfill). Consequently, like the EP, the results never represent behavior in the real environment because acid is poured through the ash, rather than dripped through it, over an extended period of time. Although the consistency of the data resulting from leachate procedures in the EP toxicity test have been improved with the TCLP, neither test produces data that simplifies what actually leaches from ash. A more accurate procedure for determining leaching characteristics would involve testing the actual leachate from an ash fill, especially a monofill that contains only waste-to-energy ash residue.

Test data for ash residue from OMS plants has been submitted to the EPA and state regulatory agencies. Lead and cadmium represent the only metals that occasionally show levels higher than the regulatory threshold in some limited samples. To simplify the following discussion, only lead will be addressed. When presenting the EP Toxicity or TCLP data, the value that is important is the upper limit of the confidence level. It is this value that is compared to the regulatory threshold and not individual sample values, even if they exceed the regulatory threshold. The most recent testing of the ash at Tulsa shows the following results for the upper band of the confidence limit on three separate analyses for EP toxicity and are for TCLP:

<table>
<thead>
<tr>
<th>EP Toxicity</th>
<th>TCLP</th>
<th>Regulatory Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (mg/l)</td>
<td>2.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

for the upper bound of the confidence limit. Of course, this means the average values were actually less.

For Marion County, a comprehensive testing program was performed in November 1986 during the facility’s energy and capacity tests. The Marion County data is particularly significant because this facility is the first in the United States using a dry scrubber and high efficiency particulate control equipment (fabric filter baghouse) on a resource recovery facility. The data from Marion County’s ash yielded the following results for the upper bound of the confidence limit on three separate analyses for EP toxicity and one for TCLP:

<table>
<thead>
<tr>
<th>EP Toxicity</th>
<th>TCLP</th>
<th>Regulatory Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead (mg/l)</td>
<td>3.4  to 4.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The tests conducted on the Bristol, Connecticut, facility, which has the same air pollution control configuration as the Marion plant, yielded similar test results. The upper bound of the confidence limit for lead was 2.5 mg/l.

OMS has performed, or has cooperatively studied with regulatory agencies, other tests on the ash from its facilities. With regard to the EP Toxicity organic substances, the levels are below the detection limit. Portions of the ash (i.e., the fly
ash) were analyzed by the EPA and determined to contain among the 
lowest levels of dioxin ever found in fly ash. These extremely 
low levels correspond to the very low levels of dioxin emissions 
achieved from the Martin GmbH stoker combustion system without 
any back-end pollution control, as well as from the stack gases 
with pollution control. 

Limited leachate data is available from existing ashfills and 
sanitary landfills. The lead levels are lower for ash monofills, 
but results from both are far below the regulatory threshold of 
5 mg/l. The data are as follows:

<table>
<thead>
<tr>
<th>Leachate Source</th>
<th>Lead (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sanitary Landfill Leachate (Malcolm Pirnie)</td>
<td>0.2 to 1.0</td>
</tr>
<tr>
<td>Ashfill Leachate (Malcolm Pirnie)</td>
<td>&lt;0.05 to 0.13</td>
</tr>
<tr>
<td>Wurzburg Ash Monofill Leachate</td>
<td>0.002 to 0.05</td>
</tr>
<tr>
<td>Sanitary Landfill Leachate (Malcolm Pirnie)</td>
<td>0.2 to 1.0</td>
</tr>
<tr>
<td>Ashfill Leachate (Malcolm Pirnie)</td>
<td>&lt;0.05 to 0.13</td>
</tr>
<tr>
<td>Wurzburg Ash Monofill Leachate</td>
<td>0.002 to 0.05</td>
</tr>
<tr>
<td>*Marion, Ore. Ash Monofill Leachate</td>
<td>0.1 to 0.6</td>
</tr>
<tr>
<td>Scandinavian Monofill Leachates</td>
<td>0.001 to 0.1</td>
</tr>
<tr>
<td>**EPA Data (Four Sites)</td>
<td>&lt;0.005 to 2.92</td>
</tr>
</tbody>
</table>

*Oregon Department of Environmental Quality
**U.S. Environmental Protection Agency data for Four Anonymous Sites

Measurements for lead and the seven other heavy metals in 
leachate from a landfill, in which both ash and raw solid waste 
have been placed (co-disposal), are well below the regulatory 
threshold(s), and have remained low over time. These lead levels 
were measured for the 1983-1987 testing of this co-disposal 
landfill leachate (in mg/10.10, 0.19, 0.06, 0.33 and 0.12). When 
ash is buried with unprocessed municipal solid waste, the 
collected leachate still has a very low lead level.

More importantly, data recently collected by the U.S. EPA 
indicate that proper monofilling of ash has a negligible impact 
on the environment. The EPA has initiated a long-term study at 
the Marion County, Oregon, ash monofill. The first year’s data 
show the leachate contained from 0.011 to 0.025 mg/l of lead. To 
determine if fugitive ash is a problem, soil samples were taken 
from around the monofill. The lead content of the soil both 
upwind and downwind of the facility contained 0.01 ppm of lead. 
Fifty-three (53) ppm lead was detected in the soil along Inter-
state 5, a few hundred meters east of the site. Background 
sample of soil east of the Interstate and far west of the faci-
lity showed levels of lead in the range of 0.014 to 0.017 ppm.

The EPA also tested for dioxins and furans in the soil around 
the monofill. The results were similar to tests conducted for 
lead. No differences between upwind, downwind, and background. 
The highest levels detected were along Interstate 5.

THE REGULATORY STATUS OF ASH

Because of the changing definition of "hazardous" waste, the 
regulatory status of municipal solid waste combustion ash has
been subject to debate over the past ten years. Prior to the Resource Conservation and Recovery Act of 1976 (RCRA), ash was primarily regulated by individual states or local jurisdictions as municipal solid waste. It was often approved as cover material for municipal solid waste sanitary landfills.

With the implementation of RCRA and the development of the federal hazardous waste management program, waste classification took on a new meaning. Congress and EPA split up the universe of waste into two categories. Those wastes, subject to management under Subtitle C of RCRA (hazardous wastes), and wastes subject to management under Subtitle D (non-hazardous wastes). Household waste and the ash residue from processing household waste were specifically excluded from Subtitle C.

This meant that household waste and incinerator ash was non-hazardous by definition. Since municipal solid waste, designated for a resource recovery facility, represents a combination of household waste and non-hazardous commercial and industrial waste, exclusion under the federal hazardous waste rules (Subtitle C) was thought to be unnecessary and therefore unavailable. Consequently, it became a requirement for the owners/operators of municipal solid waste combustion facilities to determine if their ash exhibited a hazardous waste characteristic by this difficult and onerous testing method.

When Congress enacted the Hazardous and Solid Waste Amendments of 1984, this regulatory difference between household waste and municipal solid waste ash was clarified. In this law, the ambiguous definition of "household waste" was clarified. The law states that, if a facility takes only household and non-hazardous commercial and industrial waste and has a program to prevent Subtitle C hazardous waste from being accepted, it is not deemed to be generating, treating or otherwise managing hazardous waste. In other words, the ash would not be subject to management as a hazardous waste, and testing to determine its regulatory status would not be required.

When EPA placed the law into the Code of Federal Regulations (CFR), they did not interpret it in the same way as Congress intended. EPA stated that, if the ash was tested and exhibited the characteristic of a hazardous waste, it had to be managed as such. This position has caused a great deal of confusion. If it exhibits a characteristic of hazardous waste, is the ash exempt from requirements to be managed as hazardous since it represents the by-product of municipal household waste? Or, is it to be managed as a solid waste in all cases? EPA is presently re-evaluating its decision, developing a new series of characterization tests to determine the regulatory status of ash, and developing environmentally-sound design criteria for ash burial.

Numerous states have taken similar positions. New York, Massachusetts, Tennessee and others have stated publicly that they believe the congressional clarification applies to the combined ash. The state of Oregon, well-known for some of the toughest environmental standards in the United States, believes the present testing requirements in 40 CFR 261 (which stipulates...
performance of the EP Toxicity test and other leaching procedures for hazardous wastes) are invalid for determining ash characteristics and should not be used to determine regulatory status. Other states are taking the same position. All state and federal regulatory agencies that are addressing this subject believe that efficient ash management is essential regardless of the outcome of various characterization tests.

There is no environmental exclusion from testing ash, but what is considered "efficient management" varies across the board nationwide. Consequently, regulators are developing proper ash management criteria for compliance. These criteria focus on prevention of groundwater contamination through the use of lined landfills. While monofilling ash is the most desirable option, it is probably an overly stringent requirement considering that it is unlikely that co-disposal leachate would penetrate a well-designed system, particularly one which incorporates a leachate collecting system as well as the required linings.

Both Congress and the EPA are in the process of further clarifying the regulatory status of ash and developing management standards. In numerous proposed bills, Congress has clearly stated that ash should be managed as a Subtitle D (non-hazardous) waste. In addition, all the bills require some type of lining, leachate collection, and groundwater monitoring systems for ash disposal. It is doubtful that these bills will be voted into law this session of Congress, but legislation as important as this should move in the spring of 1989.

EPA has released draft guidance on the handling, transport, storage, and disposal of ash. This guidance includes recommendations that ash containers and transport vehicles be leakproof and provided with tight coverings; that groundwater monitoring be performed at all ash disposal facilities. These liners and disposal recommendations are as follows:

- For fly ash disposed separately, disposal should be at a monofill with a double liner system.
- For combined ash or bottom ash, disposed of in a monofill, either a composite liner or a clay liner with special environmental or operating features should be used.
- For combined ash or bottom ash codisposed with garbage, a double liner or a composite liner, with pre-disposal ash treatment or source separation to reduce metals content prior to combustion is the preferred method.

ASH UTILIZATION

As discussed previously, ash contains many valuable metals and the non-metallic fraction has properties very similar to sand and gravel. These characteristics lend themselves to potential economic benefits. Ferrous and non-ferrous metal recovery using magnets, screens and other mechanical processes is used at many municipal solid waste combustion facilities worldwide. The techniques for recovery of the larger metallic components (e.g., greater than one inch) are well developed. Metals are not recovered on an industry-wide scale in the United States because
of depressed scrap metal markets (i.e., installation and operation of metal recovery equipment is dependent on local scrap metal markets). OMS investigates the local scrap markets to determine the economic viability of metals recovery from all its facilities as they enter commercial operation.

There are many metals in the ash that could only be recovered through complex and laborious processes. Metals such as cadmium, lead, zinc, copper, silver and gold are recoverable by using chemical techniques similar to those used in the minerals industry. OMS is currently investigating the feasibility of recovering these metals from the ash with various industrial concerns and research laboratories.

The major component in the ash is the inert, non-metallic fraction. Because the properties are similar to traditional aggregates, ash is commonly used as a substitute for conventional aggregate in Europe. In the mid-1970s, the Department of Transportation (DOT) researched the potential for use in the construction and maintenance of highways. Today, Marion County is pursuing the same option. In Europe, bottom ash is often used in asphaltic paving material and combined bottom and fly ash in concrete. Screened bottom ash is also used as road bed and common fill material. Perhaps, the best use of ash is as aggregate in Portland cement concrete. Municipal solid waste combustion ash has excellent properties for use in concrete itself; it is pozzolanic, which is to say it forms a weak cement-like matrix. This inherent property could be of interest to concrete block manufacturers. OMS is working with two universities to develop proper screening techniques and mixture proportions for cement blocks. Leachability of metals from the blocks will be an important issue that will require resolution before they are widely manufactured. In addition, OMS and one university are determining the likelihood of leachability of metals from the completed blocks.

There are many potentials for the use of combined ash. While the technical problems associated with the various utilization scenarios can be resolved, the institutional problems are more difficult to address (i.e., markets for the metals and public acceptance of the ash as aggregate). Lessons can be learned from Europe and Japan and other waste product utilization programs. In Japan, ash residue is used to make artificial reefs and man-made islands. Thus far, metals have not entered the food chain and subsequently pose no significant risk to aquatic life or human beings. While the United States may not necessarily need ash islands or reefs, there are many other potential uses that would fulfill material needs in the construction, manufacturing or chemical industries.

**SUMMARY**

Ash is the remaining incombustible residue representing five to ten percent by volume and 15-20 percent by weight of the municipal solid waste stream. It is a biologically inert, dense material that can be managed in a more environmentally sound manner than raw solid waste. Present testing methods do not
adequately simulate what occurs when ash is placed into a controlled landfill unit. As indicated by leachate data from actual ash fills, potential ground or surface water contamination from well-managed ash disposal units does not appear to be a problem. Before uses of combined ash can reach their fullest potential, public awareness and a better understanding of resource recovery ash characteristics is necessary. This can only be achieved through governmental leadership at state and local levels, where community education is most effective.