

Oxidative Degradation of Coals

N. C. Deno, Kenneth W. Curry, A. Daniel Jones, Robert D. Minard, Thomas Potter, Walter G. Rakitsky, and Karen Wagner

Department of Chemistry, Pennsylvania State University, University Park, PA 16802

The methods for oxidatively fragmenting coals to identifiable structures divide themselves into two types. In the more traditional type as exemplified by oxygen, permanganate, chromate, and nitric acid; benzylic hydrogen are selectively attacked. Since about half of the aliphatic hydrogens in coals are benzylic, the result of this selectivity is to destroy the aliphatic structure. In the newly discovered RO^+ type of reagent as exemplified by trifluoroperoxyacetic acid (TFPA), the aromatic rings are selectively attacked and the reagent shows great reluctance to react with benzylic hydrogen, although such hydrogen may be ultimately lost in part due to subsequent hydrogen shifts. The two types of oxidants compliment each other and provide two of the most effective methods for investigating the chemical structure of coal. Although the TFPA method is still under development, early results on 27 coals can now be presented.

Products. Aliphatic diacids and triacids of 3-8 carbons generally account for 50-90% of the observed products. Extensive model studies show that these arise from hydroaromatic-aromatic polycyclic systems. A minor fraction of these products contain OH or C=C groups. Acetic acid is the only aliphatic monoacid. It arises from arylmethyl groups in 70-80% yields and the amount of acetic acid provides the best current method for determining the %C present as arylmethyl. This value is around 1% in most coals and increases to about 3% on liquefaction of the coal. Higher monoacids such as propanoic and butanoic are not observed from which it is concluded that arylethyl and arylpropyl groups are not present in the coals.

The formation of methanol and methyl trifluoroacetate, is a measure of the amount of arylmethoxy but special precautions must be taken to trap these volatile products. These precautions were taken with a lignin and a North Dakota lignite, and 15% of the carbon was found to be present in arylmethoxy groups.

Benzene triacids and tetraacids arise from most coals. These products do not arise from TFPA oxidations of polyaromatics of 1-5 rings, polyalkyl-benzenes, or any hydroaromatic-aromatic of 2-3 rings. They do form from TFPA oxidation of 5,12-dihydronaphthacene and their formation from coals presumably reflect structures of this type in the coals.

Phthalic acid is the dominant product from TFPA oxidation of polyaromatics. It is rare or absent from the products from most coals, but becomes a major product from liquefied coals and certain aromatic coals such as PSOC-349.

Oxirane tricarboxylic and tetracarboxylic acids are major products from virtually every coal. Model studies indicate that these arise from hydro-aromatic-aromatic structures.

Pyridine polyacids are minor products and are the only products which contain nitrogen. Pyridine-3,5-dicarboxylic acid, one pyridine tricarboxylic acid, and one pyridine tetracarboxylic acid were observed. The two remaining pyridine acids are more complex and contain a carboxyl which does not esterify. Model studies indicate that these two products are polycarboxypyridine-2-acetic acids.

Divergent Coals. Six of the 27 coals give products which diverge markedly from those of the remaining 21 coals. A Texas lignite (PSOC-623) gave two unusual products which accounted for 77% of GC peak areas. These two products appear to be a carboxybiphenyl with a lactone bridge across the 2,2' positions and a product of MW 286 which could be an acenaphthenetri-carboxylic acid.

A Utah cannel coal (PSOC-155) gave anthraquinone as 82% of the GC peak areas and this one product accounted for 23% of the carbon in the coal. This coal was also unusual in that 42% of the carbon was in unbranched aliphatic chains of six or more carbons. A Kentucky Imboden coal (PSOC-372) gave anthraquinone as 43% of GC peak areas and is another divergent coal.

One coal, PSOC-349 Pennsylvania Lower Clarion, contains polycyclic aromatic structures as evidenced by phthalic acid as a major product and certain phthalides as minor products. This coal resembled liquefied coals and perhaps has been subjected to times and temperatures equivalent to liquefaction conditions.

Two Utah coals (Blind Canyon PSOC-453 and Lower Sunnyside PSOC-459) had 15% and 28% of the GC peak areas due to a product of MW 268. This product appears to contain linear aliphatic chains and is either absent or a trace product in other coals.

The above examples show that certain coals have arisen from unusual and special circumstances. This could be an unusual bioorigin or an unusual biodegradation. Only the case of PSOC-349 does the divergent nature of the products appear to arise from the effect of elevated temperature on the coal.

Conclusions. It is accepted that coal, petroleum, oil shale, and tar sands have different biological origins. The data herein indicate that some coals can have radically different biological origins relative to other coals. Generally 80% or more of the GC peak areas were due to only 10-15 products. These products had unusual, specific, and non-trivial structures. This indicates that coals still retain much of the structural specificity of their bioorigins and are fossils in the sense of chemical structure. It is suggested that for many coals most of chemical changes occurred within a few years after deposition and were the result of bacterial and fungal action. However, there are exceptions such as PSOC-349 where the aromatic nature could be a consequence of times and temperatures equivalent to the conditions of coal liquefaction.

The catalysis of chemical changes by clays and other minerals is dismissed as being ineffective in a material as non-fluid as coal. The effects of geological pressure is dismissed on the basis that the known thermal reactions of coal (liquefaction) involve bond dissociations to benzyl and other radicals. Such reactions have positive volumes of activation and will be slowed by pressure, not accelerated. In summary, the nature of the products from TFPA oxidations and their paucity along with other arguments suggest that most coals have undergone relatively little chemical change over geological time after the early changes due to decay process.

Oxidative Degradation Studies and Modern Concepts of the
Formation and Transformation of Organic Constituents of Coals and Sedimentary Rocks

Ryoichi Hayatsu, Randall E. Winans, Robert L. McBeth
Robert G. Scott and Leon P. Moore

Chemistry Division
Argonne National Laboratory, Argonne, IL 60439 USA

INTRODUCTION

In our previous oxidative degradation studies (1-4) we have suggested that:
1) In addition to aromatic rich materials, Wyoming lignite coal also contains aliphatic rich materials that are similar to type I kerogen. These aliphatic rich materials are not considered to be directly related to exinite macerals, because petrographic analysis of the coal shows a very low content of exinite ($\sim 1\%$). 2) Lignin-like polymers are incorporated into macromolecular materials of low rank coals. 3) During catagenesis (coalification processes) most of these aliphatic rich materials and lignin-like polymers are extensively transformed or degraded.

In our effort to better understand the transformation of aliphatic rich materials and lignin-like polymers during catagenesis, oxidative degradation studies of lignite, subbituminous and bituminous coals were carried out using different oxidants. For comparison with coal oxidation, Green River kerogen and softwood and hardwood lignins were oxidized. In order to determine how phenolic structures in lignins and lignin-like polymers have been altered during the evolutionary stages of diagenesis, catagenesis and metagenesis, lignin or lignite coal was heated with clay minerals to produce artificial coalification products. Since the naturally occurring low temperature transformations may require millions of years, they cannot be duplicated in the laboratory and our artificial catagenetic reactions must, therefore, be somewhat accelerated by higher temperatures (150-200°C). However, even temperatures in this range may be considered realistic, because many coals may have been subjected to such temperatures due to depth of burial (5). An oxidative degradation study of these artificial coalification products provided some evidence which helps elucidate the alteration of phenolic structures during catagenesis.

EXPERIMENTAL TECHNIQUES AND RESULTS

Sample. All samples used in this study are shown in Table 1. Prior to the oxidation reactions and other experiments, solvent soluble trapped organic materials were removed from the samples as described previously (2,6).

Oxidation. Since the oxidation procedures used have been reported in detail in our earlier work (1,2), they are described only briefly in this paper. A summary of the oxidation results is shown in Table 2. a) KMnO_4 oxidation with buffer-control: A sample (3g) methylated with d_6 -dimethylsulfate or dimethylsulfate was oxidized at 80°C with buffer-controlled permanganate (300 ml of 4.3% aq. KMnO_4 and 11.5g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) with stirring for 14-20 hours (1st step oxidation); the insoluble residue was further oxidized under the same conditions as the 1st step (2nd step). The residue of the second step was oxidized further in a third step until most of the carbon in the sample was oxidized. b) CuO-NaOH oxidation: A non-methylated sample (5g) was oxidized with alkaline cupric oxide (51.9g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 37.3g of NaOH and 185 ml H_2O) in a rocking stainless steel autoclave at 200° for 10 hours. This oxidation was carried out in a nitrogen atmosphere.

Artificial catagenesis. A mixture of sample (2.5g of lignin or lignite coal) and 0.5g of montmorillonite clay mineral pretreated with 5% HCl was dried at 100°C for 12 hours under vacuum, and was then placed in a 45cm x 2cm i.d. quartz tube sealed at one end and joined to a metal valve at the other end. The sealed end

was inserted to a depth of about 10cm in a tubular furnace which was heated at 150°C for the lignin sample and 200°C for the coal sample. These experiments were carried out in the absence of oxygen. During the heating, water and volatile materials were evaporated and condensed on the wall of that part of the quartz tube that was outside the furnace and which remained at room temperature. After the reaction, the mixture was extracted with benzene-methanol (3:1); the extract was equal to 6.3% by weight of the original softwood lignin for 14 days heating and 9.1% for 28 days heating. The insoluble residue was dried at 100°C for 12 hours; 66.3% of the carbon in the original sample remained in the insoluble residue (artificial product 1) after 14 days heating and 57.8% after 28 days heating (artificial product 2). Artificial catagenetic reaction of Wyoming lignite (100°C for 2 days, 150°C for 8 days and finally 200°C for 20 days) produced organic solvent soluble material (6.7 wt%) and insoluble residue (artificial product 3; 84.2% of carbon in the original sample).

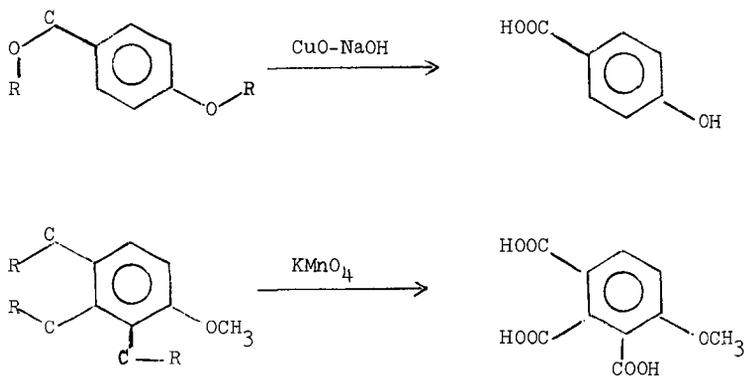
Separation and identification. Insoluble non-volatile samples or products were analyzed by solid probe MS. For each sample, about 50-70 spectra were generally taken between 25°C and 500°C. Oxidation products were esterified and analyzed by GCMS and HRMS. Non-volatile products were examined by LC, solid probe MS and HRMS.

Aliphatic rich material. In the past, a number of oxidation studies have been done to characterize the nature of aliphatic structures in coal. However, with few exceptions (7,8) only short-chain aliphatic mono and dicarboxylic acids have been reported as oxidation products. These results have suggested that non-aromatic carbon in vitrinite rich coal is present in the form of short methylene chain linkages between aromatic ring clusters, short alkyl side chains, alicyclics and hydroaromatics. For lignite coal, as previously reported (2,3), this view is no longer adequate since in the stepwise buffer-controlled permanganate oxidation products of the lignite, relatively large amounts of unbranched aliphatic dicarboxylic acids ranging from C₄-C₂₁ (with C₉ most abundant) have been identified. Branched dicarboxylic acids (C₅-C₁₀) and tricarboxylic acids (C₆-C₈) were identified also but in lower concentrations. Phthalic acid was the most abundant aromatic acid in the first step oxidation products, but benzenetricarboxylic acids (1,2,4- and 1,2,3-) were the most abundant acids in the 2nd and 3rd step oxidation products. These long-chain dicarboxylic acids identified are believed to be derived from material that is similar to type I kerogen. In the buffer-controlled oxidation of Kaiparowitz subbituminous coal, a series of unbranched aliphatic dicarboxylic acids up to C₁₄ was identified in smaller amounts than those in the lignite. The most abundant oxidation products for any of these stepwise oxidations, were the 1,2,4- and 1,2,3-benzenedicarboxylic acids. Very little or no long-chain dicarboxylic acids (C>8) were detected in the oxidation products of high volatile and low volatile bituminous and anthracite coals. However, there are some exceptions. For example, long-chain aliphatic dicarboxylic acids are produced from the oxidation (HNO₃ or Na₂Cr₂O₇) of HVC (9) and HVA (6) bituminous coals. However, these coals are cannel or cannel-like coals which are believed to have formed through different evolutionary paths from those of humic coals.

Oxidation results of Green River kerogen concentrate with buffered permanganate or chromic acid showed that more than 80% of the oxidation products are aliphatic carboxylic acids (monocarboxylic acid up to C₂₉; dicarboxylic acid up to C₂₀). The distribution pattern of these products is similar to that of the first step oxidation products obtained either from buffered permanganate or chromic acid oxidation of the lignite. CuO-NaOH oxidation of the kerogen also produced long-chain dicarboxylic acids (up to C₁₈ with max. at C₉) with lesser amounts of phenolic and benzenedicarboxylic acids. Of particular interest is the fact that this kerogen appears to be a type of kerogen resulting from contributions of both algal and higher plant materials.

Lignin-like polymer. As shown in our previous papers (1), large amounts of p-hydroxy-, 3,4-dihydroxybenzoic acids and 4-hydroxybenzenedicarboxylic acids which are regarded as lignin oxidation products were identified in the CuO-NaOH oxidation products of low rank coals. However, we have found that the same oxidation of high

rank coals gave much lower yields of phenolic acids with no predominance of 4-hydroxy isomers. Stepwise buffer-controlled permanganate oxidation of methylated lignite, subbituminous and HVC bituminous coals has been found to produce phenolic acids in good yield (in particular at the later steps) together with large amounts of benzenecarboxylic acids. It is interesting to note that, while the CuO-NaOH oxidation of these coals gives higher yields of total phenolic acids than the permanganate oxidation does, the latter generally produces more monohydroxybenzenetri- and tetracarboxylic acids as the oxidation products. This shows that the CuO-NaOH oxidation is more effective at breaking up ether bonds but much less efficient for degradation of aromatic structures bonded by C-C linkages than the permanganate is. Perhaps these phenolic polycarboxylic acids found result from the oxidative degradation of more crosslinked portions of the macromolecular structures as shown in the example below.



R= alkyl or aryl

Although many oxidation studies on lignin have been carried out, for comparison, we oxidized methylated softwood and hardwood lignins with stepwise buffered permanganate. As expected, phenolic acids were major oxidation products (see Table 2); for example, the most abundant acids obtained from softwood lignin were p-methoxy-, 3,4-dimethoxy-, 3,4,5-trimethoxybenzoic acids, 4,5-dimethoxy-1,2-benzenedicarboxylic acid and its isomers, and 4,5-dimethoxybenzenetricarboxylic acids. Benzenecarboxylic acids and short-chain aliphatic dicarboxylic acids were obtained in much smaller amounts. A few oxygen-containing heterocyclic acids were also identified in negligible amounts.

The permanganate oxidation of artificial product 1 resulted in a distribution pattern of aromatic acids produced that is intermediate between those of the lignite and the subbituminous coal. The results are that: 1) the most abundant acids are benzenetricarboxylic acids, 2) the yield of phenolic acids was 11% by wt of the total oxidation products (cf. >75 wt% for the lignins), 3) as in the case for coals, no trimethoxybenzoic acid, which is one of the major products of lignin oxidation, was found, 4) furan, benzofuran, dibenzofuran and xanthone carboxylic

acids were identified, which are found in the oxidation products of low rank coals, but not lignins; 5) no long-chain aliphatic carboxylic acids were detected. The distribution pattern of the oxidation products obtained from artificial product 2 was very similar to that of the LV bituminous coal; that is, very small amounts of phenolic acids were produced and large amounts of benzenecarboxylic acids. Benzo and dibenzofurancarboxylic acids were also found.

These results were also confirmed by solid probe MS analysis of softwood lignin and its artificial products. As expected, major mass peaks obtained from the lignin were due to mono- di- and trihydroxyphenols and their methyl and/or methoxy derivatives. On the other hand, prominent peaks from artificial product 1 consisted mainly of fragments of monohydroxyphenol derivatives and alkylbenzenes. Less intense peaks corresponding to indanes, indenenes, naphthalenes, dihydroxyphenols and oxygen containing heterocyclics were also seen. These mass spectra were very similar to those of lignite or subbituminous coals except for the lack of longer chain hydrocarbons, and N and S-containing heterocyclics. Of phenolic compounds, only monohydroxy derivatives were detected (as minor peaks) in the mass spectra of artificial product 2 as well as in the spectra of high rank coals. It is interesting to note that artificial product 3 prepared from lignite coal showed very similar analytical results (solid probe MS, IR, H/C and O/C ratios) to those of LV bituminous coal. This evidently shows that lignin-like polymers in lignite coal are extensively degraded by either natural catagenetic processes or artificial coalification reactions. It is known that during pyrolysis experiments (300-600°C) on lignin or model compounds, reactions such as demethoxylation or rearrangements of phenyl propane units, etc. can occur and furan and benzofurans (but not dibenzofuran) can be formed (10). Our artificial reactions occur at much lower temperatures, therefore, it is apparent that montmorillonite clay accelerated the catagenetic processes.

CONCLUSION

From the present and previous studies, we conclude that: 1) at least this lignite and subbituminous coal contain aliphatic rich materials which might have been derived from lipids. Such materials are no longer identifiable in higher rank coals except cannel coal, because of extensive degradation during catagenesis. Indeed, trapped volatile compounds extracted from bituminous coals are predominantly aliphatic hydrocarbons which are considered to be degradation products from the macromolecular materials. However, lignite and anthracite coals contain much less of these hydrocarbons (11,12). As Tissot and Welte (5) have also mentioned, during catagenesis aliphatic carbon chains and alicyclics in kerogen are released successively forming crude oil and gas. 2) During diagenesis and early catagenesis lignin polymers are transformed to lignin-like polymers which are incorporated into the low rank coal macromolecules. At a later stage of catagenesis, these polymers have lost their lignin-like nature as a result of continued and extensive transformation.

Higher plants are composed largely of cellulose and lignin. Lipids and lipid-like substances and proteins are also present as minor components. Lignin is more resistant to decay than cellulose which is easily removed by hydrolysis during diagenesis and early catagenesis. Thus, lignin or lignin-like polymers are preferentially concentrated together with other phenolic materials and lipids during the formation of peat and low rank coal. Since cellulose or carbohydrates are known to produce furans and benzofurans by thermal degradation at over 300°C (13,14), we may not be able to exclude the possibility that some of the oxygen-containing heterocyclics found in the structures of coal macromolecules were derived from cellulose. However, on the basis of the following results, we believe that the major source of these heterocyclics is the abundant lignin material.

We have found that artificial catagenetic reactions readily transform lignin polymers into lignin-like polymers which have oxygen-containing heterocyclic structural constituents such as furan, benzofuran, dibenzofuran and xanthone. In addition, demethoxylation of lignin structural units was found to occur easily during the reactions. Somewhat stronger conditions (longer reaction time or a little higher temperature) employed for preparation of artificial products 2 and 3, which may correspond to later catagenesis stages, resulted in additional transformation and loss of lignin-like characteristics. This may be the first clear experimental demonstration of the way that clay minerals can affect the course and result of catagenesis.

ACKNOWLEDGEMENT

This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy.

REFERENCES

1. Hayatsu, R., Winans, R.E., McBeth, R.L., Scott, R.G., Moore, L.P. and Studier, M.H., *Advances in Chemistry Series on "Coal Structure"* (Am. Chem. Soc.) in press; see also *Nature* 278, 41 (1979).
2. Hayatsu, R., Winans, R.E., Scott, R.G. and McBeth, R.L., *Fuel*, in press.
3. Hayatsu, R., Winans, R.E., Scott, R.G., McBeth, R.L., and Vandegrift, G.F., *Fuel*, in press.
4. Hayatsu, R., Scott, R.G., McBeth, R.L. and Winans, R.E., ACS, Div. of Organic Coatings and Plastic Chem., Preprint 43, 401 (1980).
5. Tissot, B.P. and Welte, D.H., *Petroleum Formation and Occurrence* (Springer-Verlag, New York, 1978).
6. Hayatsu, R., Scott, R.G., and Winans, R.E., *Oxidation of Coal in "Oxidation in Organic Chemistry"*, Part D (W.S. Trahanovsky, ed., Academic Press, New York) in press.
7. Allan, J. Ph.D. Thesis, Univ. of Newcastle upon Tyne (1975).
8. Young, D.K. and Yen, F.T., *Energy Science* 3, 49 (1976).
9. Deno, N.C., Curry, K.W., Jones, A.D., Keegan, K.R., Rakitsky, W.G., Richter, C.A., and Minard, R.D., *Fuel*, in press.
10. Sigleo, A.C., *Science* 200, 1054 (1978); see also *Geochim. Cosmochim. Acta* 42, 1397 (1978).
11. Raj, S., Ph.D. Thesis, Pennsylvania State Univ. (1976).
12. Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P., and Studier, M.H., *Fuel* 57, 541 (1978).
13. Shafizadeh, F., Sarkanen, K.V. and Tillman, D.A., *Thermal Uses and Properties of Carbohydrates and Lignins* (Academic Press, New York, 1976).
14. Brazhnikov, V.V., and Mukhin, L.M., *Chromatog. Rev.* 15, 151 (1971).

Table 1

Elemental Analysis of Samples (maf %)

No.	Sample ^{a)}	C,	H,	N,	S,	O, (by Diff.)	H/C	O/C
1	Lignite (Sheridan Wyoming)	66.4	4.8	1.5	1.1	26.2	0.87	0.29
2	Subbituminous (Kaiparowitz)	77.4	5.6	1.2	0.3	15.5	0.87	0.15
3	HVC bituminous (IL #2)	73.9	5.2	1.4	2.4	17.1	0.84	0.23
4	Softwood lignin ^{b)}	65.6	5.9	<0.1	<0.1	28.5	1.08	0.33
5	Hardwood lignin ^{b)}	63.1	5.8	<0.1	<0.1	31.1	1.10	0.37
6	Artificial product 1	69.7	5.2	<0.1	<0.1	25.1	0.90	0.27
7	Artificial product 2	78.3	5.0	<0.1	<0.1	16.7	0.77	0.16
8	Artificial product 3	84.3	4.9	1.3	0.9	8.6	0.69	0.08
9	Green River kerogen	77.5	10.1	2.4	1.4	8.6	1.56	0.08

a) For samples not listed here, see Ref. 1. b) Samples provided by Dr. R.J. Preto, (North Carolina State University, Raleigh)

Table 2

Summary of Buffer Controlled Permanganate^{a)} and CuO-NaOH^{b)} Oxidation Products

Sample wt % ^{c)}	1	2	3	4	5	6	7	9
Organic acids	52.1 (35.3)	41.3	51.5 (19.6)	19.3	21.2	57.2	52.1	57.8 (20.3)
Humic Acid-like material	25.1 (55.3)	16.8	45.4 (62.5)			21.6	20.3	
Insoluble residue ^{d)}	14.2 (11.0)	37.6	11.3 (21.0)	26.3	27.1	14.5	30.3	(49.3)
Wt% of Identified Acids								
Aliphatic Dicarboxylic Acid <C ₇	11.0 (1.8)	9.5	6.3 (1.0)	2.5	2.2	4.3	2.4	11.8 (13.2)
Aliphatic Dicarboxylic Acids ≥C ₈	14.2 (0.8)	9.7	1.1 (<0.1)	<0.1	<0.1	<0.1	<0.1	69.3 (53.0)
Phenolic acids	11.3 (66.6)	10.4	8.3 (54.1)	87.3	74.8	11.0	1.5	3.4 (8.6)
Benzenecarboxylic Acids	54.7 (26.0)	55.3	58.9 (36.2)	7.6	13.5	58.4	70.3	5.2 (9.3)
Oxygen-containing Heterocyclic Acids	6.7 (<1.0)	5.8	6.2 (<1.0)	<1.0	1.3	7.8	4.9	<0.1 (<1.0)
Others	2.1 (3.8)	9.3	19.2 (7.7)	2.6	8.2	18.5	20.9	10.3 (14.9)

a) Total amounts (wt%) of 3 step oxidation products are shown.

b) Data obtained from CuO-NaOH oxidation are shown in parentheses.

c) Wt% was obtained from a sample on a dry, ash free basis. Elemental analysis showed the presence of ash (1.5-5%) in organic acid fraction and humic acid-like material respectively.

d) Insoluble residue consists of non-oxidized sample and partially oxidized material which is not soluble in solvents; wt% was estimated from carbon analysis of the residue.

e) Wt% was estimated from the GC. For non-volatiles, solid probe MS and HRMS were used.

f) Polynuclear aromatic, S- and N- containing heterocyclic, aliphatic monocarboxylic acids and unidentified compounds.

Blank spaces represent isolations and identifications that have not been done or for which experimental results have not yet been obtained.

OXIDATION OF COAL: A MECHANISTIC PUZZLE

Sujit Kumar Chakrabartty

Alberta Research Council
11315 - 87th Avenue
Edmonton, Alberta, Canada
T6G 2C2

INTRODUCTION

All coals, other than anthracites, tend to be very sensitive to oxidation. Even exposure to air at ambient temperature causes deterioration to the extent that properties such as solubility, caking, fluidity, tar-yield, etc., are adversely affected. Although the loss of heating value and decrease in tar-yield due to oxidation can be explained in terms of loss in hydrogen contents, details of the chemical changes and the mechanism of oxidation are uncertain. There is agreement among coal chemists that the initial stages of air-oxidation involve chemisorption of oxygen at readily accessible surface sites, but further definition of the mechanistic path at the molecular level is still controversial.

Air-oxidation renders coal increasingly soluble in alkali as 'humic acid' with ultimate loss of 20-30% carbon as carbon-oxides and 40-50% hydrogen as water. The solubilized coal, named as 'humic acid', is spectroscopically similar to the parent coal except for oxygen functional groups identified as phenolic -OH, -COOH, and =CO (ketone and/or quinone) respectively. The peripheral molecular changes associated with the formation of oxygen-functions are explained (1) by a scheme resembling the gas-phase oxidation of naphthalene to phthalic acid and maleic anhydride in sequential steps. The limiting elemental compositions of the humic acids depend on the temperature of oxidation, and tend to vary slightly with coal rank. Higher temperature and/or higher oxygen partial pressure accelerates the rate of the reaction. At temperatures beyond 250°C, a virtual low-temperature combustion process sets in.

It could be argued that production of phthalic anhydride by gas-phase oxidation of naphthalene is a catalytic process, and requires temperature-pressure conditions far more severe than coal-oxidation. Coals, in contrast, weather away under ambient conditions, leaving chemically identical 'humic acid' that can be generated by air-oxidation at 150-200°C. The reactivity of coal for electrophilic attack by oxonium ions is therefore hardly comparable to that of naphthalene, and it is unlikely that the mineral matter in coal is a more effective oxidation catalyst than vanadium pentoxide.

The formation of transient ketones or quinones during air-oxidation is indirectly demonstrated by 'ammoxidation' of coal. If the reaction is conducted in an atmosphere of gaseous ammonia (2), the rate of reaction falls rapidly with progressive incorporation of nitrogen (as high as 20%), and the reacted solid resists further oxidation. In the postulated mechanism for this reaction, the transformation of transient ketonic functions to nitrogen functions in the form of amide or imide, and further stabilization of imido functions by oxidative ring-closure, are

put forward to explain the refractory nature of the "amoxidation" product (2b). The ketones may be generated by oxidation of hydroxyl groups, insertion of oxygen in C-H bonds, or by oxidation of carbanion species.

The presence of alkali, e.g. sodium hydroxide, on the other hand, accelerates rate of reaction. When coal is slurried with aqueous sodium hydroxide and reacted with oxygen under pressure (and temperature as high as 200°C), a complete break-down of structural components lead to aromatic carboxylic acids (3). Thirty to 45 per cent of the total carbon is recovered as carboxylic acids, and the remainder is lost to carbon dioxide. No attempt was made to demonstrate a mechanistic route for this process. However, reactions of coal with sodium dichromate at 250°C in an autoclave under autogenic pressure (4), or with sodium hypochlorite in an open flask at 60-65°C (5), also destroy the structural components to yield low-molecular weight carboxylic acids. In all these reactions, the oxidation paths appear to be substantially identical, (if one considers the generation of the products only), and the carbon distributions in the products at the completion of the reactions are quite similar. While the reactivity for oxidation decreases with increasing rank, such dependence is eliminated if the sample is partially air-oxidized or 'weathered'. This can be rationalized from the generation of ketones in the hydrocarbon skeleton of coal, which, in turn, would activate adjacent carbon atoms for further oxidation. The step-wise oxidative degradation of hydrocarbon chains (6) is supposed to follow this course. However, coal is not an agglomeration of hydrocarbon chains and a better mechanism (based on a strictly physical model) can be developed from the concept of a 'shrinking core'. The oxidant is chemisorbed and reacts on the surface. With air, the predominant process is rapid generation of humic acid followed by secondary decomposition of carboxyl functions as envisaged by Jensen et al (7) and elaborated by Berkowitz (1). In wet oxidation, the 'humic acid' formed at the outer layer of the particle is extracted, and further oxidized in a homogeneous solution phase; and a fresh reactive surface is created on the shrinking particle for continuing 'primary' oxidation.

But such a phenomenological description does not in itself offer clues to a mechanistic path at the molecular level. It merely defines questions that need to be answered, specifically,

- a. what are the active surface sites (and their chemical properties) at which initial oxidation occurs?
- b. does the reaction involve radical or ionic species, or does it proceed by simple insertion of the electrophilic agent?
- c. which bonds are cleaved to generate low molecular-weight compounds? and
- d. why is the reactivity of the oxidant insignificant in relation to the reactivity of the coal?

SEARCH FOR A PROBE

In coal-constitution studies, oxidants, thought to be selective, were used to explore the mechanistic maze of coal-oxidation. However, in the classical work of Bone and Wheeler (8) which was based on alkaline potassium permanganate, the oxidant cleaved aromatic as well as aliphatic C-C bonds. Later work was devoted to study the effect of milder oxidants. For example, aqueous performic acid (9) readily converts coal into humic acid (which was quite helpful because the humic acid on reduction with sodium amalgam yielded distinctive phenolic products in which propyl-benzene structure of lignin could be identified). Sodium dichromate (4), and sodium hypochlorite (5), intended for reactions with aliphatic structures, readily cleaved some coals to products much less complex than humic acid and yielded benzene polycarboxylic acids as major products. The study with dichromate was restric-

ted to hvb-coals, whereas, with hypochlorite from lignite to lvb-coal (C=90%) were reacted. Partial oxidation of aromatic structures by dichromate ions was suspected along with the intended cleavage of aliphatic C-C bonds. The mechanism of hypochlorite oxidation is not fully understood. The reactivity of coals toward hypochlorite oxidant is rank-dependent. Reaction with coal containing more than 82% C is limited to surface degradation; loses 5-12% carbon presumably as CO₂; and the resulted solid residue has higher oxygen content than the parent coal. Yet, if the high-rank coals are pretreated with nitronium tetrafluoroborate (a nitrating agent), or are partially oxidized with air at 150°C, complete dissolution of coal can be achieved.

Pretreatment with a nitrating agent should yield conventional nitrobenzene derivatives. The nitro-group generally deactivates aromatic rings for electrophilic attack, and activates the side chain for oxidation. Derivatization might therefore be expected to confine oxidation to aliphatic structures and to preserve aromatic rings. But only 3-6% of the nitrogen of the nitro-coal could be recovered after hypochlorite oxidation, and the product-mixtures contained quite insignificant amounts of nitro-benzene structures (10).

The puzzle was unscrambled when it was observed that high rank coals could be more extensively oxidized when the hypochlorite was used in a two-phase (methylene chloride-water) system, and tetrabutylammonium fluoroborate was added as a phase-transfer catalyst. Table 1 shows the results of this study.

Table 1. Two-Phase Hypochlorite Oxidation: Recovery of Carbon in Products (per cent carbon)

Products	hvb-coal (C 86, H 5.5)	lvb-coal (C 88.1, H 4.9)
Carbon dioxide	13.2	22.04
Volatile acids (a)	1.8	3.0
Hexane soluble (Me-ester)	10.0 (b)	11.0 (c)
Hexane insoluble (Me-ester)	1.3	2.5
MeOH-soluble (acid)	9.0	14.1
Unaccounted	10.0	10.0
Oxidized insoluble residue	44.7	27.3

(a) acetic, chloroacetic, propionic and malonic acids; (b) phthalic acid, 94%; (c) phthalic acid 62%, tricarboxylbenzene 32% and tetracarboxylbenzene 5%.

It is noteworthy that in this system lvb-coal is oxidized to a greater extent (giving high yield of carbon dioxide and methanol-soluble acids), than hvb-coal. Structural differences between these two coals are also revealed in the respective product distributions. From the hvb coal, phthalic acid is a major product (in addition to carbon dioxide), and a substantial fraction (44.7% C) resists further oxidation by this reagent. From the lvb-coal, major products are di-, tri- and tetracarboxylbenzene; carbon dioxide yield is 50% greater and only 27% carbon resist further degradation.

In a parallel study of oxidation under the same conditions, a polymer, ethyl-polyvinylbenzene, was found to be unreactive in an uncatalyzed as well as in a catalyzed two-phase system. Even after nitration with nitronium tetrafluoroborate, it did not, like coal, break down to carbon dioxide or chloropicrin. Only discoloration and partial chlorination were observed. The reactivity of coal toward this oxidant was found to be very much greater than the reactivity of benzylic methylene or methine groups in ethyl-polyvinylbenzene polymer.

The catalyzed oxidation with hypochlorite ions of coal may not be restricted

to aliphatic structures only. Permanganate ions in the form of alkylammonium salts in pyridine solution have been used to oxidize aliphatic side-chains (11). Three coals, subbituminous, hvb and lvb, were treated with an excess of tetrabutylammonium permanganate in pyridine at 50°C and yielded results summarized in Table 2.

Table 2. Oxidation with Tetrabutylammonium Permanganate

Oxidation Data	Coal		
	subbit (C 78%)	hvb (C 86%)	lvb (C 88%)
% Carbon recovered as soluble product	9.5	6.2	11.3
Products, mole %			
Acetic acid	12.4	11.4	11.5
Propanoic acid	3.3	4.9	2.3
Butanoic acid	-	3.9	-
Pentanoic acid	yes	4.5	yes
Succinic acid	-	17.4	yes
Glutaric acid	-	0.7	-
Adipic acid	-	3.0	-
Octanedioic acid	86.1	50.5	84.2
Phthalic acid	-	3.5	-
Unknown peak	yes	yes	yes

The mole percent compositions were calculated from the major identified peaks in the gas chromatograms of the methyl esters. The unknown peak in the chromatogram was assigned as 1,1,2-ethanetricarboxyl acid from mass-spectral data and retention time. The yield of this acid from hvb coal was greater than from the other two; and, if the structural assignment is correct, the isolation of this product indicates the presence of bridged aliphatic configurations in the parent coals. In contrast, the large-component in the acid mixture was octanedioic acid (which must have derived from ring structures larger than cyclohexane) and is present in lesser quantity (50% as compared to 84-86%) in hvb coal. Moreover, only the hvb coal yielded succinic, glutaric and adipic acids, presumably by degradation of cyclohexane rings. The straight chain components, derived from oxidation, are almost identical in all three coals. Though the total conversion yields are in the order of 10% only, the data are very significant to indicate the structural differences between coals. The concept of systematic evolution of rank by increasing aromatization of hydroaromatic structures is too empirical to accommodate the results of this study. The presence of bridged alicyclic and large alicyclic rings in the hvb coal is demonstrated by these results; further attention would focus to establish whether these structural features are unique from some coals or belong to a set pattern of coal-constitution.

CONCLUSION

The above discussion justifies the theme of the presentation. Coal-oxidation is unique in a mechanistic sense, but much more complicated than would be expected from oxidations of standard organic compounds. It is reasonable to assume that aliphatic structures, particularly benzylic methyl, methylene or methine groups, or carbon adjacent to hetero-atoms are the most reactive, and are oxidized to ketones or carboxylic acids. In order to degrade coal to CO₂ and water-soluble low-molecular-weight compounds by mild oxidants, an abundance of these functional groups must be assumed. However, the stability of ethyl-polyvinylbenzene polymer towards hypochlorite oxidant indicates that activation of coal-carbon for

oxidation results from features other than electronegativity of aromatic rings. The uniqueness of the coal-oxidation has to rest on a destabilizing factor which makes even aromatic sites vulnerable.

One may speculate that mineral matter in coal is coordinated with aromatic structures, and that the resultant complexes are destabilized by electrophilic attack. If a coal is an entangled interpenetrating macromolecular mixture (12), the destabilizing effect would decrease with increasing compactness of the physical structure which accompanies increase in rank; higher rank coals would therefore be less reactive. However, if the oxidant can also, like mineral matter, intercalate, it would open the structure up, and produce destabilization. The success of wet oxidation would then depend less on the oxidation potential than on the ability of the oxidant to intercalate. The oxidation of lvb coal with assistance from phase-transfer catalysts in a two-phase system is consistent with this view.

EXPERIMENTAL

The subbituminous and lvb coals are from Alberta, Canada (Cretaceous), and hvb coal is from Virginia, U.S.A. (Carboniferous). All coals are cleaned by gravity separation.

Commercial bleach (0.8 molar solution) was used for hypochlorite oxidation. Tetrabutylammonium fluoroborate was of electrometric grade supplied by Southwestern Analytical Chemicals Inc., Austin, Texas.

Tetrabutylammonium permanganate was prepared by exchange reaction between tetrabutylammonium bromide and analytical grade potassium permanganate.

Two-phase Oxidation

5.0 g air-dried coal and 5.0 g tetrabutylammonium fluoroborate were placed in a 50 ml dichloromethane, and the suspension agitated in an Erlenmeyer flask at 30°C while hypochlorite solution was added at intervals until consumption of the oxidant ceased. The reaction required three days from completion. The reaction mixture was then further diluted with dichloromethane, and separated into layers. The organic layer contained the ammonium salt and was removed. The aqueous layer, after acidification, was extracted with ethyl ether. Solid products filtered from the aqueous layer were extracted with methanol. The ether-soluble fraction was methylated with diazomethane, and the esters were separated into hexane-soluble and -insoluble fractions. The composition of the hexane-soluble fraction was determined by G.C.-mass spectrometry.

Oxidation with Tetrabutylammonium Permanganate

5.0 g dried coal, 20.0 g oxidant, and 75 ml pyridine were heated in a two-necked flask under helium atmosphere at 50°C, and mechanically stirred for 24 hours. The solvent was then distilled off under reduced pressure, and the residue diluted with water. Excess permanganate was neutralized with sodium bisulfite; the mixture acidified with hydrochloric acid, and finally filtered. The water-extract was washed with dichloromethane to separate tetrabutylammonium salt, and thereafter continuously extracted with ethyl ether. The ether-extract was methylated with diazomethane and analyzed by G.C.-mass spectrometry.

REFERENCES

1. N. Berkowitz, An Introduction to Coal Technology, Academic Press, New York, Chap. 5 (1979).
- 2a H. M. Brown and N. Berkowitz, A.I.Chem.E., Chem. Engng. Progr. Symp. Ser., 64, 85, 89 (1968).
- 2b S. K. Chakrabartty and N. Berkowitz, Fuel 48, 151 (1969).
3. R. S. Montgomery and E. D. Holly, Fuel 36, 63, 493 (1957);
ibid, 37, 181 (1958).
4. R. Hayatsu, R. E. Winans, R. G. Scott, L. P. Moore and M. H. Studier,
Organic Chemistry of Coal (ed. J. W. Larsen), ACS Symp. Ser. 71,
Chap. 7, 108 (1978).
5. S. K. Chakrabartty, ibid., Chap. 6, 101 (1978).
6. R. L. Whistler and R. Schweiger, J. Am. Chem. Soc. 81, 5190 (1959).
7. E. J. Jensen, N. Melnyk, J. C. Wood and N. Berkowitz, Adv. Chem. Ser. 55,
621 (1966).
8. W. A. Bone and L. Quarendon, Proc. Roy. Soc. 110A, 537 (1926);
ibid, 148A, 492 (1935).
9. J. Bimer, P. H. Given and S. Raj, ACS Symp. Ser. 71, Chap. 5, 87 (1978).
10. S. K. Chakrabartty, unpublished work.
11. T. Sala and M. V. Sargent, J. Chem. Soc. Chem. Comm., 254 (1978).
12. N. Berkowitz, Proceed. R. A. Welch Foundation Conf. XXII, Chemistry of
Future Energy Resources, Chap. III, 75 (1978).

A Novel Method for Controlled Oxidation*

Ben M. Benjamin and Vernon F. Raaen

Chemistry Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830

The purpose of this paper is to describe a novel method for the oxidative degradation of coal or other organic material. The procedure is potentially useful for structure determination. As originally conceived, this method was intended for use with aqueous potassium permanganate as oxidant, but it is equally applicable with other oxidizing agents. Sodium hypochlorite can be substituted for KMnO_4 except that controlling the pH and monitoring the end point become more difficult. Results with potassium permanganate only will be described here but sodium hypochlorite was tried. An advantageous feature of the method is the simultaneous removal of soluble products from further contact with oxidizing agent as the oxidizing agent attacks the substrate. In principle, the experimental approach resembles that of column chromatography.

Any oxidative degradation of a natural product for structure determination is of little use if carried out too far; for example, to the smallest, most oxidation-resistant materials such as carbon dioxide, acetic acid, and benzoic acid. Potassium permanganate oxidations of reactive species such as coal and kerogen are particularly difficult to control. Partially oxidized fragments which go into solution can be attacked more effectively than the solid starting phase, a situation which results in loss of structural information. Bone and coworkers,² as well as Djuricic,³ in their classic works, attempted to preserve labile products by conducting stepwise partial oxidations. These procedures are cumbersome and involve numerous manipulations to remove unreacted starting material and manganese dioxide. Another difficulty is that phenolic materials^{4,5,6} can undergo coupling reactions thus generating larger molecules and giving misleading results due to a larger number of substituents.

The procedure is quite simple. An example is described for the degradation of coal. Illinois #6 vitrain (100 g ground to $< 250 \mu\text{m}$) was mixed with 100 g of Celite #503, and the mixture was ground further in a ball mill. The resulting powder was then mixed with 800 g of Celite. This mixture was poured into a glass column 5 cm by 130 cm which contained a pad of sand and a pad of Celite 6 cm thick on a coarse sintered-glass support. A 600-ml reservoir on top of the column was filled with a saturated aqueous solution of potassium permanganate. About 10 days was required to percolate the solution (790 g of KMnO_4 in 15 l of water) through the column. Although the reaction requires little attention, the time can be reduced considerably by reducing the pressure at the receiver. The course of the reaction could be followed by the heat detected in a 5-cm band as the reaction progressed down the column. The reaction was terminated when permanganate color appeared in the Celite pad at the bottom of the column. The oxidation was nearly complete; the coal left on the column weighed only 4 g and could be made to react with only 5 g of KMnO_4 . Recovery of the unreacted material gave about 1 g of a black solid that resembled amorphous carbon and that contained 0.4 g of HF-soluble siliceous material. The alkaline effluent from the column was extracted with ether; the extract contained a negligible amount (≈ 0.05 g) of neutral material. The volume of alkaline solution was reduced to 500 ml by means of a rotary evaporator, chilled on ice, and acidified with cold 6 N aqueous HCl. The accompanying

*Research sponsored by the Office of Fossil Energy, U. S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

evolution of CO₂ stopped after the addition of 2.0 to 2.1 moles of HCl. The carboxylic acids were removed by continuous ether extraction for 150 hr to afford 52.7 g of carboxylic acids. After ether extraction the aqueous phase that remained was heated at 40°C./50 Pa to remove the water. The residual dried and crushed salts were extracted by percolating boiling tetrahydrofuran through them for 24 h. Vacuum distillation of the tetrahydrofuran left 24 g of a tacky almost-black material that readily absorbed moisture from the air and had a caramel-like odor. A small sample of that material was exchanged once with D₂O, pumped dry, and again dissolved in D₂O for n.m.r. measurements on a 100-MHz instrument. The n.m.r. spectrum showed five broad peaks between 1.4 and 5 ppm. The chemical shifts were measured with respect to Me₄Si (external). The spectrum consisted of a small peak at 1.4 ppm, large peaks at 1.85 and 3.68 ppm, and intermediate sized peaks at 4.35 and 4.95 ppm. The material, which contained hydroxylated aliphatic acids, was not investigated further.

One aliquot of the ether-extracted acids was partially distilled. Another aliquot was converted to the ¹⁴C-methyl esters for analysis on a gas chromatograph equipped with a radioactivity monitor. Normal aliphatic acids through butyric acid were isolated along with the dibasic oxalic, succinic, 2-methyl succinic, and glutaric acids. The n.m.r. spectrum indicated the presence of malonic and pimelic acids, but those acids could not be isolated in amounts sufficient for identification by other means. The aromatic acids: benzoic; *o*-, *m*-, and *p*-phthalic; 3-methyl phthalic; 4-methyl phthalic; hemimellitic; and trimellitic were found. Formic, acetic, oxalic, succinic, and trimellitic acids were most abundant. Van Krevelen⁷ considered it significant that benzoic acid had not been found in a single case where conventional oxidation procedures were used, but we showed by isotope dilution that a small amount of benzoic acid was formed in the single stage oxidation of Illinois #6 vitrinite using potassium permanganate. In this study, attempts to isolate mellitic acid (benzenehexacarboxylic acid) by the method of Bone *et al.*² were unsuccessful. The yield of CO₂ in the percolation procedure is much less than the approximately 40% reported by Bone *et al.*²

Efforts to economize on the use of Celite were disastrous — the pressure produced by *in situ* generated manganese dioxide invariably burst the tubes. No difficulty was experienced when at least 8 to 10 parts (w/w) of Celite was mixed with 1 part of the ground coal. Flow rates were also improved by the higher Celite-to-coal ratios.

Not all coals are adaptable to this procedure; North Dakota lignite (PSOC-246) is usually oxidized through the first 15 cm of the column, and then the flow stops. The plugging of the column might be caused by the formation of Al(OH)₃ or by chemical comminution of the coal which may produce the layer of black substance that forms on the sintered-glass support. Materials that are soluble in a non-reactive solvent are easily dispersed in Celite by tumbling them together with the solvent and Celite in a rotary evaporator and then removing the solvent under vacuum. This method of dispersal was used in the oxidation procedure described⁸ for 4-methyl-2,6-di-*tert*-butylphenol, a compound found⁹ to be loosely bound to Yallourn brown coal. It is interesting to compare the results of a batch oxidation of the above hindered phenol with the results of the controlled column (or percolation) oxidation. A brief account is given here and further details can be found in Ref. 8. Batch oxidation of 4-methyl-2,6-di-*tert*-butylphenol gave principally the two dimers, 4,4'-ethylene-bis[2,6-di-*tert*-butylphenol] (λ) and 2,2',6,6'-tetra-*tert*-butyl-1,1'-stilbenequinone (λ') and a smaller amount of another dimer 2,6-di-*tert*-butyl-4-(3',5'-di-*tert*-butyl-4'-hydroxybenzyl)-4-methyl-2,5-cyclohexadiene-1-one (3), Figure 1. Although small amounts of other compounds were isolated, it is obvious that further oxidation would give derivatives of λ , λ' , and 3, reflecting their structure rather than that of the starting material.

The controlled oxidation of 4-methyl-2,6-di-tert-butylphenol did not give dimers in the column effluent. A small yield of a mixture of neutral compounds was isolated. These compounds, 4, 5, 6, 7, 8, 9, 10 are described in Fig. 2. The acid fraction contained formic acid, acetic acid, and pivalic acid and a mixture of hydroxy and keto acids which could not be separated.

Compound 4 contains a CH₂ group. It probably is derived from the aromatic ring accompanied by hydrogen migration. Compounds 5, 6, and 7 are the result of ring contraction while 8, 9, and 10 are more like the original material.

Although the latter results demonstrate the complex nature of interpreting oxidation results in terms of structure, we believe the method presented has valuable potential. The scope of the method should be extensively investigated with other oxidizing agents and model compounds, and we offer our initial results for a start in that direction.

REFERENCES

1. The method was originally conceived by Vernon F. Raaen, Inorganic and Organic Section Bimonthly Reports, Chemistry Division, ORNL, Aug. 11, 1975, p. 12; Feb. 12, 1976, p. 27; June 14, 1976, p. 15.
2. Bone, W. A., Horton, L. and Ward, S. G. Proc. of the Royal Soc. (London) Series A 1930, 127, 480.
3. Djuricic, M. V., Vitorovic, D., Andresesen, B. D., Herz, H. S., Murphy, R. C., Preti, G. and Biemann, K. Advances in Organic Geochemistry, (Eds. H. R. v. Gaertner and H. Wehner) Pergamon Press, New York, 1972, p. 305.
4. Dryden, I. G. C. in Chemistry of Coal Utilization, Suppl. Vol. (Ed. H. H. Lowry) John Wiley, New York, 1973, Ch. 6, p. 272.
5. Yohe, G. R., Hill, D. R., Dunbar, J. E. and Scheidt, F. M. J. Am. Chem. Soc. 1953, 76, 2688.
6. Taylor, W. I. and Battersby, A. R. Oxidative Coupling of Phenols, Marcel Dekker, New York, 1967.
7. Van Krevelen, D. W. Coal, Elsevier, London, 1961, p. 227.
8. Benjamin, B. M., Raaen, V. F., Hagaman, E. W. and Brown, L. L. J. Org. Chem. 1978, 43, 2986.
9. Swann, P. D., Harris, J. A., Siemon, S. R. and Evans, D. G. Fuel 1972, 52, 154.

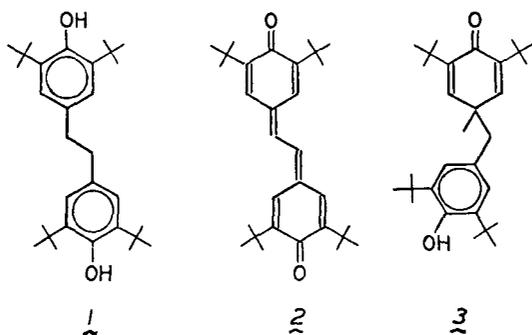


Figure 1. Products of batch oxidation of 4-methyl-2,6-di-tert-butylphenol with potassium permanganate.

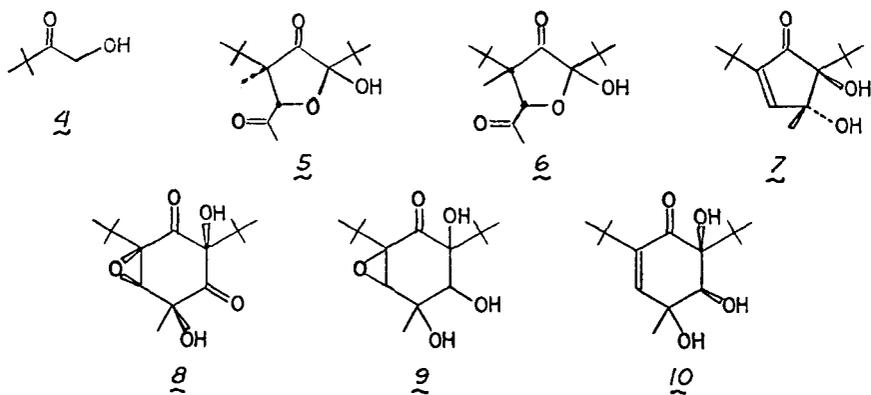


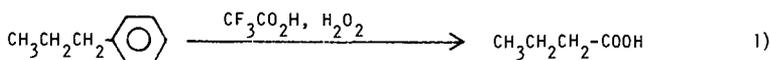
Figure 2. Products of column oxidation of 4-methyl-2,6-di-tert-butylphenol with potassium Permanganate

THE FATE OF SULFUR FUNCTIONS ON OXIDATION WITH PEROXYTRIFLUOROACETIC ACID

Clifford G. Venier, Thomas G. Squires, Yu-Ying Chen,
Juliana C. Shei, Robert M. Metzler, and Barbara F. Smith

Ames Laboratory*, Iowa State University, Ames, Iowa 50011

Oxidation has long been one of the primary tools used to probe the chemical structure of coal(1). The newest method is that developed by Deno, who reported that, while the aromatic portions of molecules were rapidly degraded by reaction with hydrogen peroxide in trifluoroacetic acid, the aliphatic skeleton is relatively inert to the reagent (2,3,4), equation 1). In contrast, classical oxidants, such as potassium permanganate or potassium dichromate, are known to preferentially oxidize the aliphatic portions of alkylated aromatics, equation 2). Deno claimed that this



new degradation will be useful in the determination of coal structure and has recently published structural studies based on peroxytrifluoroacetic acid oxidations (5-9).

We believe that this oxidation might be very useful in the determination of the kinds and amounts of organic sulfur functional groups in coal, based on the following considerations:

1. Of all the functionalities proposed for coal (see Figure 1), those containing divalent (sulfide) sulfur are likely to be the most nucleophilic.
2. With a powerfully electrophilic oxidant, such as peroxytrifluoroacetic acid, the most nucleophilic atoms, the sulfurs, will be the most readily oxidized.
3. The functionalities resulting from the oxidation of divalent sulfur, namely sulfones and sulfonic acids, are electron-withdrawing groups.
4. Since the mechanism of the electrophilic oxidation of aromatic rings involves the rings as sources of electrons, electron-withdrawing substituents, in particular, $-\text{SO}_2\text{R}$ and $-\text{SO}_3\text{H}$, will retard the oxidation of rings to which they are chemically attached.

On the basis of these assumptions, we would expect aromatic rings directly attached to sulfur in coal to survive less than exhaustive oxidation and appear in the products as sulfones and sulfonic acids. Since the rest of the aromatic structure of coal will be completely oxidized, the higher molecular weight portion of the products should be enriched in compounds containing sulfur (see Figure 2).

Table 1 shows that the assumption that sulfur compounds are rapidly oxidized is true for most sulfur functions. Dibenzothiophene and diphenyl disulfide are

*Operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

exceptions, but under the conditions reported by Deno, they, too, are oxidized to the tetravalent state. The oxidation of dibenzothiophene to its dioxide was also recently reported by Liotta and Hoff(10), who also found that pyridines are oxidized to their N-oxides by peroxytrifluoroacetic acid. That tetravalent sulfur-bearing rings are less susceptible to oxidation can be seen in Table 1. Benzenesulfonic acid, diphenyl sulfone and dibenzothiophene are not oxidized under conditions, 5 hours at 60°C, which, according to Deno, oxidize alkyl benzenes. The point is further illustrated in Table 2 which shows the fate of ω -phenylalkyl phenyl sulfides ($n=0-3$). Decreasing yields of sulfones and increasing yields of the ω -carboxyalkyl phenyl sulfones signal increasing amounts of oxidation of the ring remote from sulfur as n goes from 0 to 3.

We believe that the anomalously large amount of benzenesulfonic acid observed in the oxidation of phenylethyl phenyl sulfide ($n=2$) arises from a more facile elimination of benzenesulfonic acid from phenylethyl phenyl sulfone than from the corresponding sulfones in the other cases. Benzenesulfonic acid would disproportionate (11) or oxidize(12) or both under the reaction conditions to yield benzenesulfonic acid. In fact, phenyl benzenethioisulfonate, the other product of the disproportionation is also observed in the reaction mixture, even though it would be expected to be itself relatively easily oxidized to benzenesulfonic acid

Finally, the assumptions upon which we based our tentative hypothesis that the peroxytrifluoroacetic acid oxidation might be useful in the determination of the chemical nature of organic sulfur in coal having been demonstrated, we turned our attention to coal itself (Illinois #6) and its pyridine extract. Figure 3 shows two gc traces of the CH_2N_2 -methylated products from the oxidation of coal by peroxytrifluoroacetic acid. Both FID and sulfur sensitive FPD detector traces are shown. While we have not yet identified these materials, we have demonstrated that compounds containing sulfur can be identified among the products of the peroxytrifluoroacetic acid oxidation of coal.

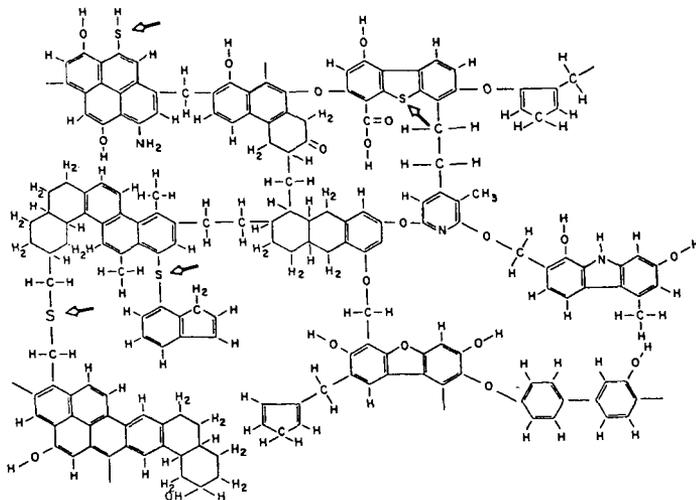


Figure 1. Modified Wiser Coal Structural Model

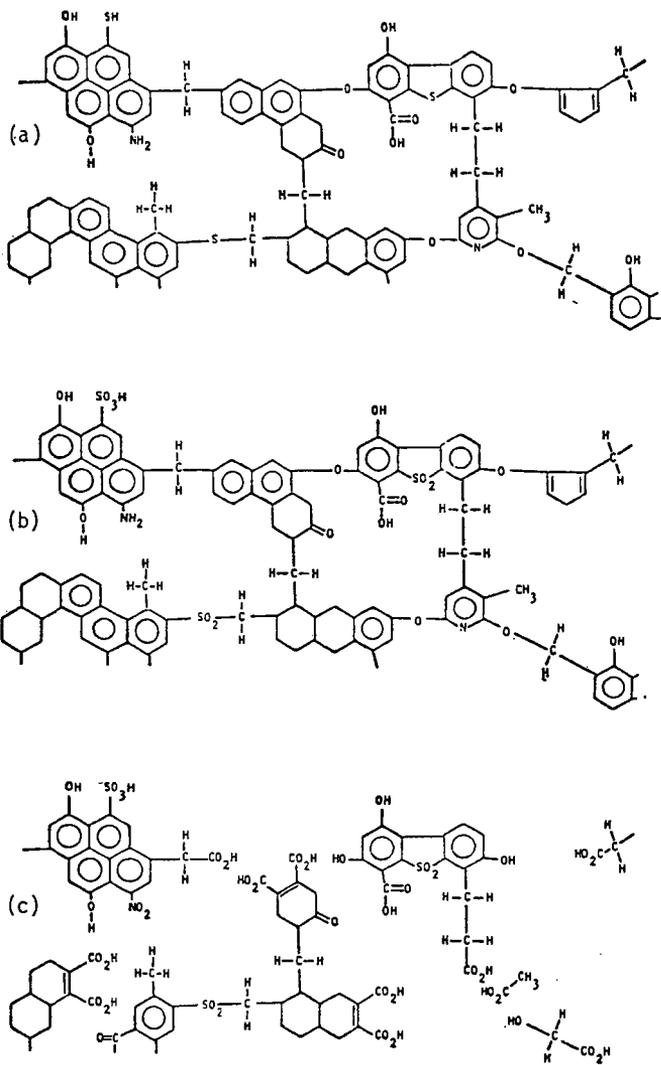


Figure 2. Proposed Effect of Peroxytrifluoroacetic Acid Oxidation on Coal Structure: (a) unmodified, (b) after partial oxidation, and (c) after extensive oxidation.

EXPERIMENTAL

All sulfides were used as obtained from commercial sources, except phenyl 2-phenyl-ethyl sulfide, which was prepared by the reaction of sodium benzenethiolate with 2-phenylethyl chloride. Trifluoroacetic acid, 30% hydrogen peroxide and 90% hydrogen peroxide were used as supplied. Infrared spectra were taken on a Beck nm Model 4230 or IBM FTIR/90 series spectrophotometer as KBr discs. Nuclear magnetic resonance spectra were taken at 60 MHz on a Varian Em-360A spectrometer.

Oxidation of Sulfides with Peroxytrifluoroacetic Acid: Trifluoroacetic acid and hydrogen peroxide were mixed at 0°C, the sulfide added with cooling, and the temperature of the reaction mixture adjusted to the desired temperature with a water bath. At the end of the reaction time, the reaction was poured into water and a small amount of platinum on asbestos or platinum on carbon was added to destroy excess peroxide. This step often required several hours. When the mixture proved negative to starch-KI paper, the excess trifluoroacetic acid and water was removed on a rotary evaporatory, the final vestiges of solvent and water removed at high vacuum on a vacuum line, and the mixture dissolved in methanol and treated with diazomethane in ether. The resulting mixture of neutral compounds and methylated acids was injected on to an OV 101/Chromasorb W-HP column (8'x1/4"). Compounds were identified by retention times and coinjection and quantitated by the internal standard method.

Oxidation of Coal and Coal Extract with Peroxytrifluoroacetic Acid: A mixture of trifluoroacetic acid and 90% hydrogen peroxide was prepared at 0°C. The coal or coal extract (0.25g) and 15 ml of the peroxytrifluoroacetic acid mixture were placed in a round-bottomed flask fitted with a dropping funnel into which was placed an additional volume of the peroxytrifluoroacetic acid mixture. The flask was heated in a water bath, and, at about 50°-60°C, a vigorous exothermic reaction began. As the reaction subsided, additional oxidant was added from the dropping funnel. This procedure was continued until the exothermic reaction had stopped. The coal samples consumed much more oxidant than did the extracts. The reactions were then worked up in the same manner as for the sulfides, except that it was necessary to filter mineral matter from the oxidized coal sample and it was not necessary to use platinum to destroy excess peroxide.

Table 1. OXIDATION OF COMMON ORGANIC SULFUR FUNCTIONAL GROUPS WITH $\text{CF}_3\text{CO}_3\text{H}$.

COMPOUND	PRODUCTS (% yield)	
	$\text{CF}_3\text{CO}_3\text{H}/\text{H}_2\text{O}_2$, 25°, 15 min	$\text{CF}_3\text{CO}_3\text{H}/\text{H}_2\text{O}_2$, 60°, 5 h
Ph-SH	Ph-SO ₃ H (53%) Ph-S-S-Ph (5%) Ph-S-SO ₂ -Ph (5%)	Ph-SO ₃ H (92%)
Ph-S-S-Ph	Ph-S-S-Ph (91%) Ph-SO ₃ H (5%)	Ph-SO ₃ H (94%)
(n-butyl) ₂ S	(n-butyl) ₂ SO ₂ (99%)	(n-butyl) ₂ SO ₂ (99%)
dibenzothiophene	a	dibenzothiophene-5,5-dioxide (91%)
Ph-S-Ph	Ph-SO ₂ -Ph (95%)	Ph-SO ₂ -Ph (92%)
Ph-S-CH ₂ Ph	Ph-SO ₂ -CH ₂ Ph (99%)	Ph-SO ₂ -CH ₂ Ph (92%)

^a partially oxidized, sulfide still detectable.

Table 2. OXIDATION OF ω -PHENYLALKYL PHENYL SULFIDES WITH $\text{CF}_3\text{CO}_2\text{H}$ ^a

n	$\text{PhSO}_2(\text{CH}_2)_n\text{Ph}$ sulfone yield	$\text{PhSO}_2(\text{CH}_2)_n\text{COOH}$ sulfone acid yield	PhSO_3H sulfonic acid yield
0	92%	0%	0%
1	91.5%	0.5%	0%
2	55%	8%	16%
3 ^b	32%	16%	1%

^a $\text{CF}_3\text{CO}_2\text{H}/\text{H}_2\text{O}_2 = 1.13/1$, 60° , 5 hr, see experimental for work-up procedure.

^bAt least 10 other compounds containing sulfur can be observed in the gc trace using flame photometric detection. If each is assumed to have one sulfur and an FID response factor which is the average of the sulfone and the sulfone acid, they would account for $37 \pm 12\%$ of the sulfurs.

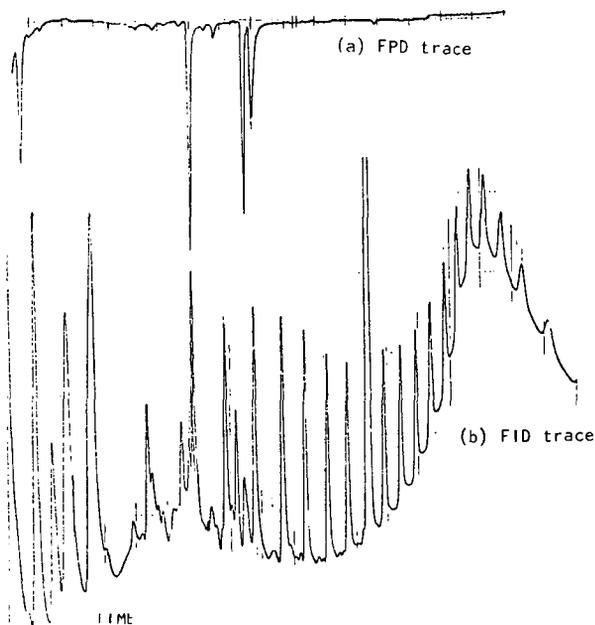


Figure 3. Gas Chromatogram of CH_2N_2 -Methylated Product of the Oxidation of Illinois #6 Coal by Peroxytrifluoroacetic Acid.
(a) Flame Photometric Detector; (b) Flame Ionization Detector

REFERENCES

1. For an excellent review of the area, see R. Hayatsu, R. G. Scott and R. E. Winans, "Oxidation of Coal," in Oxidation in Organic Chemistry. Part D, W. S. Trahanovsky, ed., Academic Press, New York, in press. We wish to thank the authors for providing a copy of their manuscript in advance of publication.
2. N. C. Deno, B. A. Greigger, L. A. Messer, M. D. Meyer, and S. G. Stroud, Tetrahedron Lett., 1703-4 (1977).
3. N. C. Deno, B. A. Greigger, and S. G. Stroud, Fuel, 57, 455-9 (1978).
4. N. C. Deno, B. A. Greigger, and S. G. Stroud, ACS Div. Fuel Chem., PREPRINTS, 23, 54-7 (1978).
5. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, and S. G. Stroud, Electric Power Research Institute AF-960, Project 779-16, Final Report, May, 1979.
6. N. C. Deno, K. W. Curry, J. E. Cwynar, A. D. Jones, R. D. Minard, T. Potter, W. G. Rakitsky, and K. Wagner, ACS Div. Fuel Chem., PREPRINTS, 25, #4, 103-10 (1980)
7. N. C. Deno, K. W. Curry, B. A. Greigger, A. D. Jones, W. G. Rakitsky, K. A. Smith, K. Wagner, and R. D. Minard, Fuel, 59, 694-8 (1980).
8. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, K. A. Smith, and R. D. Minard, Fuel, 59, 699-700 (1980).
9. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, D. D. Whitehurst, and T. O. Mitchell, Fuel, 50, 701-3 (1980).
10. R. Liotta and W. S. Hoff, J. Org. Chem., 45, 2887-90 (1980).
11. J. L. Kice and K. W. Bowers, J. Am. Chem. Soc., 84, 605-10 (1962)
12. C. J. M. Stirling, Int. J. Sulfur Chem., B, 6, 277-320 (1971).

EVIDENCE FOR LONG-CHAIN ALIPHATIC STRUCTURES IN SPORINITE
KEROGEN BY ALKALINE POTASSIUM PERMANGANATE OXIDATION

J. Allan⁽¹⁾ and S. R. Larter⁽²⁾

- (1) GeoChem Laboratories (Canada) Ltd., 3650 - 21 Street N.E., Calgary
Alberta, Canada T2E 6V6
(2) Union Oil Company of California, P.O. Box 76, Brea, California,
92621, U.S.A.

INTRODUCTION

Microscopical examinations of kerogens have shown that many coal macerals are not restricted to coal swamp depositional environments, but are in fact widespread in occurrence, in many types of sedimentary rocks. Exinites in particular are of geochemical interest, for they have been implicated in crude oil generation under certain circumstances⁽¹⁻³⁾. They are also common components of coals of diverse ages⁽⁴⁾. The work reported here represents a part of a study undertaken to compare chemical similarities and differences between different macerals⁽⁵⁾ and outlines the results of oxidative degradation of a series of sporinite concentrates isolated from Carboniferous coals of high-volatile bituminous rank.

SAMPLES AND ANALYTICAL METHODS

A series of sporinite concentrates were prepared from selected coals by a combined crushing, heavy liquid ($ZnCl_2$) flotation technique, modified after the method of Dormans *et al*⁽⁶⁾. Final concentrate purities ranged from 77-95% of sporinite, with the main contaminants being inertinites. The samples cover the rank range 0.5-1.1% R_{max} (equivalent to vitrinite carbon contents of 77-87%). Prior to oxidation, all samples were extracted with a chloroform: acetone: methanol mixture (47:30:23 v/v) and then saponified with a solution of KOH in methanol (5% w/v).

The oxidation procedure was taken from the kerogen oxidation method of Djuricic *et al*⁽⁷⁾, whereby the sporinite was dispersed in an excess of 1.6% KOH solution at 80°C and an aliquot of potassium permanganate was added (the ratio of sporinite: oxidant varied between 4:1 and 1:1 in different experiments). After consumption of the oxidant, the mixture was filtered, and residual sporinite was returned to the reaction vessel for a second oxidation step, this procedure being continually repeated until no further oxidation took place. Filtrates from each oxidation step were acidified to pH 1 and the resultant brown to black precipitates were removed. Residual solutions were extracted with diethyl ether to recover organic-soluble acid fractions, which were then methylated with diazomethane. The esters were fractionated by preparative thin-layer chromatography (0.5 mm SiO_2 plates, developed in petroleum ether: ether 9:1), and resulting mono- and dimethyl ester fractions were analyzed by temperature-programmed gas chromatography.

RESULTS AND DISCUSSION

Pertinent data concerning the samples and oxidation products are given in Table 1.

TABLE 1
Rank and Oxidation Product Data for Sporinite Kerogen

Sample	Rank \bar{R}_{\max} %	Oxidation Products		Ratio Coal/Oxidant (w/w)	Number of Oxidation Steps
		Monobasic Acids (as Me esters) (ppm)	Dibasic Acids (as di-Me esters) (ppm)		
A	0.51	740	4060	4:1	13
B	0.60	640	15670	4:3	7
C	0.63	460	17970	1:1	6
D	0.68	720	21510	1:1	6
E	0.91	1160	12890	4:1	20
F	1.04	470	16080	1:1	7
G	1.12	610	16470	1:1	7

The distributions of straight-chain compounds in both the mono- and dibasic chromatographic fractions showed several progressive changes as the rank of the sporinites increased, and also as oxidation progressed within individual sporinites. Initial oxidation steps of low-rank sporinites (samples A-D) yielded complex mixtures of acids (range C_n - C_{28}) dominated by normal, saturated, even-carbon-numbered components with 14-20 carbon atoms. In later oxidation steps, normal acids became increasingly predominant and contained increasing proportions of long-chain (C_{20}) homologues, which eventually become the dominant products. The long-chain compounds showed a slight predominance of C_{22} , C_{24} , C_{26} and C_{28} acids. At ranks higher than 0.9% \bar{R}_{\max} (samples E-G), products were confined mainly to the range C_n - C_{18} with prominent straight-chain constituents, and the C_{18+} fraction was seen in trace amounts only.

The main aliphatic products in the dibasic chromatographic fraction were straight-chain, saturated α,ω -dicarboxylic acids in the range C_n - C_{28} , although homologues higher than C_{15} were always minor components and were confined to the lower rank samples. Individual compound concentrations decreased regularly with increasing chain length from maxima at C_8 or C_9 . With increasing sample rank, the concentration of α,ω -dicarboxylic acids in the dibasic fraction decreased progressively, and at the highest ranks, virtually no recovery of these compounds was obtained.

The monobasic acids are produced by oxidative cleavage of an n -alkyl moiety bonded to the kerogen structure at one end of the chain. The nature of the function involved is unknown, except that esters are unlikely since all the samples were saponified prior to oxidation. The saponification procedure yielded low quantities of fatty acids (10 ppm) and n -fatty acids above n -C₂₂ were not produced. No α,ω -dicarboxylic acids were produced(5). Further, functional group analyses of coals indicate that carboxyl groups do not survive into the bituminous rank range(8). The n -alkyl moieties exhibit some characteristics which indicate derivation directly from the original plant lipids. Long-chain (C₂₀) n -acids are probably derived from original plant waxes, which show a strong predominance of even-carbon-number chains in modern plants. Coalification processes have modified the original distribution so that the even-dominance has been almost smoothed out. Such a smoothing out process of original biolipids has been demonstrated many times in the solvent-soluble fractions of sedimentary organic matter, including coals(9-11). The short-chain (C₂₀) n -acids have distributions indicating derivation from fats, particularly the predominance of n -C₁₆ and n -C₁₈. These compounds are similar in distribution to simple alkyl degradation products of sporopollenin, a natural biopolymer found in modern exine walls(12), suggesting that this material may contribute to the structure of fossilized sporinite.

The α,ω -dicarboxylic acids are produced by diterminal oxidative cleavage of polymethylene chains within the kerogen. The nature of the original terminal structures is unknown, but alkylated mono- and diaromatic hydrocarbons bearing n -alkyl substituents of similar chain lengths have been observed in the pyrolysis products of some of these sporinites(13). Polymethylene chains have been found in a wide variety of sedimentary organic materials, frequently with chain lengths extending beyond C₂₀(14-17). In an extreme case, the exinite maceral alginite (*Botryococcus* type) is composed of significant amounts of a highly cross-linked polymethylene chain network(18,19). In the majority of published data, the distribution of chain lengths in the polymethylene structures does not suggest direct incorporation of simple lipids with the retention of original structures. Thus, it is thought that during the diagenetic alteration stage, the incorporation of functionalized lipids into a developing geopolymer takes place in such a way that biological identity is lost, possibly by chain fragmentation or cross-linking. Laboratory simulation of such a process has been carried out, whereby artificial melanoidins (representing polyfunctional proto-kerogen) have been reacted with standard alkenes, acids and alcohols (representing lipids)(20). Data obtained to date suggest that a specific compound, for example n -hexadecanol, reacts with the melanoidin in a complex manner which produces an homologous series of chemically bonded alkyl moieties with chain lengths shorter than the original structure.

While the origin of the polymethylene structures is speculative, the oxidation data show that they are not stable under advancing coalification, and are progressively lost from the kerogen at successively higher ranks. The evidence further suggests that they are expelled as complete entities, for there is no good indication of progressive chain shortening with increasing rank.

SUMMARY

n-Alkyl moieties are present in at least two modes in sporinite kerogen, although they represent very small proportions of the total structure. Singly-bonded "peripheral" alkyl chains have been found, with chain length distributions which suggest direct incorporation of fats and waxes from the original plants. Coalification slowly modifies the structures so that specific biological identities are slowly obliterated. Diterminally bonded polymethylene chains are also present, and these structures are thought to develop during early diagenesis through complex reaction pathways involving functionalized lipids and poly-functional substrates.

The oxidation data suggest that oxidizable n-alkyl moieties are slowly expelled from the kerogen matrix, for recoveries decline as the rank of the sporinite increases. However, caution must be exercised in interpreting data from a single degradation technique, for pyrolytic degradation yielded significant quantities of n-alkanes from all the sporinite kerogens. Thus, it would appear that further n-alkyl moieties must be present, but incorporated in a manner which is not susceptible to alkaline permanganate oxidation.

ACKNOWLEDGEMENTS

Much of this work was carried out at the University of Newcastle, England, as part of doctoral dissertation (JA) under the guidance of Dr. A. G. Douglas, and was funded by the Natural Environment Research Council.

REFERENCES

1. Brooks J.D., and Smith J.W. Geochim. Cosmochim. Acta (1969), 33, 1183.
2. Powell T.G., and McKirdy D.M. Am. Assoc. Petrol. Geol. Bull. (1975), 59, 1176.
3. Connan J. and Cassou A.M. Geochim. Cosmochim. Acta (1980), 44, 1.
4. International Handbook of Coal Petrography (1963), 2nd Edition. C.N.R.S. (Paris)
5. Allan J. Unpublished Ph.D. thesis (1975). University of Newcastle upon Tyne.
6. Dormans H.N.M., Huntjens F.J. and van Krevelen D.W. Fuel (1957), 36, 321.
7. Djuricic M.V., Murphy R.C., Vitorovic D. and Biemann K. Geochim. Cosmochim. Acta (1971), 35, 1201.
8. Blom L., Edelhausen L. and van Krevelen D.W. Fuel (1957), 36, 135.
9. Brooks J.D. and Smith J.W. Geochim. Cosmochim. Acta (1967), 31, 2389.
10. Leythaeuser D. and Welte D.H. In: Adv. Org. Geochem. 1968. Eds: Schenck P.A. and Havenaar I. Pergamon Press (Oxford) 1969. PP 429-442.

11. Allan J. and Douglas A.G. Geochim. Cosmochim. Acta (1977), 41, 1223.
12. Brooks J. and Shaw G. Nature (1968), 219, 532.
13. Larter S.R. and Allan J. Paper to be presented during ACS Symposium on Organic Geochemistry of Coal (this meeting).
14. Robinson W.E., Heady H.H. and Hubbard A.B. Ind. Eng. Chem. (1953), 45, 788.
15. Hunneman D.H. and Eglinton G. In: Adv. Org. Geochem. 1968. Eds: Schenck P.A. and Havenaar T. Pergamon Press (Oxford) 1969, PP 157-166.
16. Djuricic M.V., Vitorovic D., Andresen B.D., Hertz H.S., Murphy R.C., Preti G. and Biemann K. In: Adv. Org. Geochem. 1971. Eds: von Gaertner H.R. and Wehner H. Pergamon Press (Oxford) 1972. PP 305-322.
17. Simoneit B.R. and Burlingame A.L. Geochim. Cosmochim. Acta (1973), 37, 595.
18. Larter S.R. Unpublished Ph.D. thesis (1978). University of Newcastle upon Tyne.
19. Allan J., Bjoroy M. and Douglas A.G. In: Adv. Org. Geochem. 1979. Eds: Douglas A.G. and Maxwell J.R. Pergamon Press (Oxford). In press.
20. Larter S.R. and Douglas A.G. Geochim. Cosmochim. Acta. In press.

OXIDATIONS OF ILLINOIS NO. 6 COAL AT AND BELOW 60°C

Frank R. Mayo and Lee A. Pavelka

SRI International, Menlo Park, CA 94025

INTRODUCTION.-- The objective of our research program is to determine the nature of the singly-bonded connecting links between the condensed aromatic and hydroaromatic ring systems in Illinois No. 6 coal. Our approach has evolved as the work has progressed. We started with separate investigations of (1) the toluene-insoluble, pyridine-soluble (TIPS) fraction (about 2/3) of the 16% of this coal that can be extracted by pyridine and (2) the 84% that is insoluble. We have used the TIPS fraction as a model for the insoluble fraction and have investigated several cleavage reactions by changes in molecular weight, all at temperatures at or below 50° to avoid changes in the carbon skeleton. (1) We conclude that the number-average molecular weights (M_n) can be reduced to about 1/3 of the initial values by cleavage of ether and ester groups. However, such reactions have succeeded in dissolving only about 10% of the pyridine-insoluble fraction and therefore much of the effort described in this paper was directed toward dissolving, by oxidation, the maximum proportion of the pyridine-insoluble fraction with a minimum loss of carbon, for further chemical and spectroscopic investigation.

In the course of this work, we found that extraction of the pyridine-extracted coal with benzylamine ($BnNH_2$) at 100° would dissolve an additional 14% of the coal (on the original unextracted coal) and then that ethylene diamine + dimethylsulfoxide would dissolve an additional 15%, to produce extracts that were largely or entirely soluble in pyridine, and insoluble fractions that would swell to increasing extents in pyridine. This progress report also includes some oxidations of $BnNH_2$ -extracted coal, carried out with the idea that the smaller and less tightly crosslinked insoluble fraction should lose less carbon on oxidation.

The principal products of all of our oxidations are black acids, sparingly but completely soluble in water at pH 7 or above to give dark solutions, and almost completely insoluble at pH 3 or below. Other products are light-colored acids that are so soluble that they are difficult to separate from sodium chloride, and undissolved coal. Yields are given on the basis of carbon recovery and the loss is mostly, and assumed to be wholly, carbon dioxide.

EXPERIMENTAL.-- To minimize further oxidation of dissolved material, reactions were carried out in steps, at the ends of which the undissolved material was extracted with dilute aqueous base, often at 60°, with separations by centrifuging, until the washings became light-colored. The insoluble material was then reoxidized, but only after drying in the K-O-t-Bu experiments. All the soluble material was combined, filtered through a very fine fritted filter, concentrated at about 20 torr, acidified, collected, washed with very dilute HCl, and dried. Oxidations with oxygen were followed by oxygen absorption. (2) Oxidations with aqueous NaOCl (household bleach) were carried out with gradual additions of reagent to the bottom of the reaction tube, where the coarsest material would collect. The reaction in a 30° bath was followed by the amount of 5N NaOH required to maintain the pH at 13 (about 0.5 NaOH/NaOCl consumed), or by the self-heating on addition of NaOCl containing this proportion of NaOH in addition to that required to bring the pH of the NaOCl solution to pH 13.0. The rate of oxidations decreased as the spent NaOCl solution accumulated. In the HNO_3 oxidations, the acid was removed by water washing of the insoluble coal after each step and the soluble material was then extracted with aqueous base. The water-soluble organic products were recovered from the HNO_3 washings.

In general, the water-soluble acids were determined from the carbon contents of the dried acid-NaCl washings but in an experiment similar to NaOCl oxidation 3, this residue was methylated and the proton NMR was determined in chloroform: 26% methoxy, 38% other aliphatic, 21% benzyl and 15% aromatic. When these results are recalculated, substituting H atoms for methyl in methoxy, these acids would contain 11% carboxyl and phenol hydrogen atoms, and a little more aliphatic than benzyl plus aromatic hydrogen atoms. Further, a few milligrams of nearly colorless oil was isolated from the esters by microdistillation; microanalysis gave 48.36% C, 5.23% H, 1.1% N, and H/C = 1.29.

This H/C ratio is surprisingly low for methyl esters of an acid containing mostly aliphatic and benzyl groups and is consistent with earlier suggestions that Illinois No. 6 coal (3) and Wyodak solvent-refined coal (4) contain condensed alicyclic rings.

Rates of Oxidation.-- Rates of oxidation depended on the state of subdivision of the extracted coal, -325 U.S. mesh with pyridine-extracted coal, -60 mesh with BnNH₂-extracted coal. However, the finest material would oxidize first and fastest and the coarser residue with BnNH₂-extracted coal was often dried and ground between steps. Rates are compared in Table 1.

The initial reaction of 0.7M NaOCl with wet pyridine-extracted coal at pH 13 and 30°C is obviously exothermic and too fast to measure conveniently. The next fastest oxidation is with oxygen and K-O-t-Bu in dimethyl sulfoxide (DMSO) at 30° but this rate depends on the amount of base present. The rates of oxidation decrease as the base is consumed and eventually reach a nearly constant rate, about 0.25 mmole O₂/hour in 21 g of DMSO solution, nearly independent of the amount of coal left in suspension between 0.1 and 1.0 g. The rate is restored to as high as 20 mmole O₂/hr by addition of more K-O-t-Bu. However, most of the black acids produced are insoluble in DMSO and must be washed out with water. Then the insoluble coal must be dried before the next step.

Oxidations with oxygen in suspension in water at pH 13 and with 34% nitric acid are next fastest. Slowest are oxidations 6 and 7 with oxygen in pyridine with azobis(2-methylpropanitrile) as initiator and t-BuO₂H as promoter. (2) These oxidations are self-retarding.

NaOCl No. 21 and oxygen No. 8 were run with different portions of the same dispersion of pyridine extract in water. The TIPS fraction was dissolved in pyridine and precipitated by water, then washed with water and collected by centrifuging. The NaOCl oxidation was fast. The oxygen oxidation was slow and became slower; after three steps, 52.3% of the C remained undissolved and 11.1% had been lost as CO₂. The recovered TIPS fraction was redispersed in water by way of a pyridine solution and then oxidized much faster and nearly completely, with little loss. The significance of these results is not clear.

Products of Oxidation.-- Products of oxidation are described in Table 1. In discussing the relations between the oxidizing agents and conditions and the products of oxidation, several factors should be considered.

(1) Substrate. With both NaOCl (20 and 23) and O₂ (2 and 9), BnNH₂-extracted coal gave less black acids and more losses than pyridine-extracted coal. The TIPS fraction of pyridine-soluble extract reacted more completely and gave higher yields of black acids than the extracted coal with either oxidizing agent.

(2) Basicity. NaOCl appears to react by two mechanisms (3), a selective high-pH reaction of acidic hydrogen whose rate increases with pH and toward which the black acids are relatively stable, and an unselective low-pH reaction that involves a large variety of organic substrates, including black acids, and ends with oxidation-stable carboxylic acids. The selective mechanism probably involves hypochlorite ion, the other, unionized HOCl, chlorine, or the intermediate in the NaOCl-NaClO₂ disproportionation. (3) The rate of oxidation of a water suspension of extracted coal with oxygen also increases with pH near pH 13 and becomes very fast in DMSO in the presence of K-O-t-Bu.

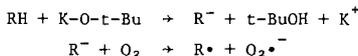
(3) Yields of Black Acids. Superficially, all the black acids are similar in color and solubility. The yields are limited by the amount of coal that oxidizes sufficiently to dissolve in weak base, the loss of carbon, presumably as CO₂, and their lower resistance to further oxidation by NaOCl below pH 12.

(4) Composition of Black Acids. As has been shown elsewhere (3), the extensive oxidation of pyridine-extracted coal by NaOCl at pH 10 (No. 3) results in a large increase in carbonyl, a preferential loss of aromatic carbon, and a large increase in H/C in the black acids formed. In black acids formed with less loss of carbon, changes in H/C ratios and in solid state ¹³C NMR spectra are smaller, but the product of HNO₃ oxidation 1 has the most aromatic and carbonyl carbon, the least ether and alcohol carbon, and by far the lowest H/C ratio, showing preferential destruction of aliphatic material. A NaOCl product like 20 and the DMSO product 11 are almost identical by NMR, but the latter product has the higher H/C ratio, indicating preferential loss of aromatic material. In oxidations of the pyridine-soluble extract, neither oxidation 8 or 21

resulted in much change in H/C, at least partly because of low loss of CO₂.

MECHANISMS.-- Oxidations in pyridine of both pyridine-extracted coal and the TIPS fraction of the extract with free-radical initiator and added t-BuO₂H (to restrict termination reactions to t-BuO₂• radicals) (2) is slow, incomplete, and inefficient in cleaving coal molecules or fragments. In the conventional free radical-chain mechanism, the -CH₂- and -CH₂O- links are much less reactive than the hydroaromatic and polynuclear structures (5).

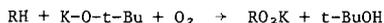
The mechanism proposed for the oxidation of coals in aqueous NaOH at 50 to 100°C by Kapo and Calvert (6) appears to be applicable to our oxidations in with K-O-t-Bu. The initiating steps are:



The two-step chain cycle is then:



but each cycle also requires an equivalent of base in the production of the required R⁻ by the first initiating step. The net result for the initial stage of the oxidation is:



However, for breakage of C-C bonds, further and more complicated steps are required.

We have proposed (3) that aromatic rings with phenol groups are most susceptible to attack by NaOCl at pH 13. Similar reactions may also be involved in oxygen oxidations with strong base.

SUMMARY.-- The Introduction showed that Illinois No. 6 coal can be largely converted to soluble material by cleavages at ether and ester bonds, without loss of carbon, at or below 50°C. For further breakdown of connecting links in both dissolved and undissolved fractions, several oxidation methods are effective at 30 to 50°C. Aqueous NaOCl gives the fastest and most complete reaction and some of the lowest losses as CO₂. 34% nitric acid is most selective in attacking aliphatic material (connecting links); the yield of black acids can probably be improved by use of more and shorter oxidation steps between separations of oxidation products. The highest selectivity in the removal of aromatic material was in NaOCl oxidation 3 at pH 10, but with high loss of carbon. Oxidation with K-O-t-Bu in DMSO also appears to remove aromatic material preferentially but the change in H/C ratio is limited by low formation of CO₂.

Selective oxidation at low temperatures appears to have great potential for making coal soluble at low temperatures for further investigation, with only 10 to 20% loss of carbon, either by preferential destruction of connecting links or of key rings in condensed systems (perhaps leaving most of the aliphatic connecting links intact). A combination of F₃C-CO₂H, H₂O₂, and H₂SO₄ is notable for removing aromatic material from coal (6), but its potential in making coal soluble with minimum loss of carbon is unknown to us.

ACKNOWLEDGEMENT.-- This research was supported by the U.S. Department of Energy through the Pittsburgh Energy Technology Center under Contracts No. ET-78-C-01-3293 and AC22-78ET11423. Discussions with the Contract Monitor, Dr. Sidney Friedman, have been helpful.

REFERENCES

1. F. R. Mayo, D. H. Buchanan, and L. A. Pavelka, Preprints, Division of Fuel Chemistry, 25(2), 182 (1980).
2. J. G. Huntington, F. R. Mayo, and N. A. Kirshen, Fuel, 58, 24 (1979).
3. F. R. Mayo and N. A. Kirshen, Fuel, 58, 698 (1979).
4. D. D. Whitehurst, M. Farcasiu, T. O. Mitchell and J. J. Deckert, Jr., The Nature and Origin of Asphaltenes in Processed Coals, Electric Power Research Institute, Palo Alto, CA, p. 7-110, July 1977.
5. J. G. Huntington, F. R. Mayo, and N. A. Kirshen, Fuel, 58, 31 (1979).
6. N. C. Deno, B. A. Greigger, and S. G. Stroud, Fuel, 57, 455 (1978).

TABLE 1

OXIDATIONS OF COAL FRACTIONS IN WATER SUSPENSION
(except as noted)

Experiment No.	Coal fraction	Oxid. agent	Temperature, °C	Initial concn.	coal, g/ml	Steps	21		23		9		11 ^c		7 ^c		2		6 ^c		8		1	
							Pyridine extract	Pyridine extract	Pyridine-extracted	Benzylamine-extracted	DMSO	Pyridine	Pyridine	H ₂ O	Pyridine	Pyridine	H ₂ O	Pyridine	Pyridine	Pyridine	Pyridine	Pyridine	Pyridine	Pyridine
		← 0.7M NaOCl →																						
		← H ₂ O →																						
		← Decreasing from 0.3 →																						

FOURIER TRANSFORM INFRARED STUDIES OF COAL OXIDATION

Paul Painter and Carol Rhoads

Materials Science and Engineering Department
Steidle Building
The Pennsylvania State University
University Park, PA 16802

INTRODUCTION

It is well-known that even minor amounts of oxidation can dramatically change the properties of caking and coking coals. In a number of studies (1,2) it has been noted that there is an increase in the reactive oxygen groups, -OH, COOH and C=O, upon low temperature oxidation. However, in recent work (1,3-5) changes such as the loss of swelling properties of coking coals upon low temperature oxidation have been attributed to the formation of ether cross links. In fact, Wachowska, et al. (5) could determine no change in the carbonyl content of Balmer 10 coal upon oxidation at 100°C, using chemical methods of analysis.

In contrast to these results, an FTIR study of the weathering of a Canadian coking coal (6) and preliminary work on the laboratory oxidation of a caking coal (7,8) demonstrate that carbonyl and carboxyl groups are formed in the early stages of the oxidation. In this paper we will report further studies of coal oxidation by FTIR, with particular emphasis on the detection of hydroxyl groups and the changes that occur in reacting oxidized coal with potassium in THF.

RESULTS AND DISCUSSION

The utility of FTIR in the study of the oxidation of coal is illustrated in Figure 1, which compares the infrared spectrum of a sample of unoxidized PSOC 337 coal to the spectrum of the same sample subsequent to heating in air at 150°C for two hours. A weak shoulder appears near 1690 cm^{-1} upon oxidation. All spectra were recorded on a Digilab FTS 15B spectrometer using 400 'scans' (co-added interferograms) at a resolution of 2 cm^{-1} . Figure 1 also shows the difference spectrum obtained by subtracting the spectrum of the unoxidized sample from that of the oxidized. The criteria used to determine the "correct" degree of subtraction was the elimination of the kaolinite bands at 1035 and 1010 cm^{-1} , since this clay should be relative unaffected by low-temperature oxidation. It can be seen that this subtraction results in the elimination of the aromatic C - H stretching mode near 3050 cm^{-1} and the aromatic C - H out-of-plane bending modes between 700 and 900 cm^{-1} . This is to be expected in that direct oxidative attack of the aromatic nuclei is unlikely under the oxidation conditions used in this study and confirms the choice of kaolinite bands as a subtraction standard.

In contrast to the aromatic C - H bands, the aliphatic C - H stretching modes near 2900 cm^{-1} appear negative, or below the baseline, demonstrating a loss in CH_2 groups upon oxidation. This observation is not particularly novel, as methylene groups in the benzylic position are well known to be sensitive to oxidation and are probably the initial site of oxidative attack. However, the difference spectrum reveals new detail in the 1700 to 1500 cm^{-1} region of the spectrum. The 1685 cm^{-1} band, which appeared as a weak shoulder in the original spectrum of the oxidized coal, is now resolved as a separate band. Furthermore, a prominent new band near 1575 cm^{-1} is now revealed in the difference spectrum. This band is not detectable in the original spectrum. The 1685 cm^{-1} absorption is probably due to an aryl alkyl ketone, while the 1575 cm^{-1}

mode can be assigned to an ionized carboxyl group, COO^- .

In addition to the difference bands at 1685 and 1575 cm^{-1} , there is a weak broad absorption centered near 1200 cm^{-1} . This band was not differentiated from background scatter at lower levels of oxidation (7,8). Modes in this frequency range are usually assigned to aromatic C-O stretch, as in phenols or ethers. However, there are a number of other functional groups that absorb in this region of the spectrum (e.g., O-H bend, various CH_2 bending modes), so that specific assignments cannot be made unambiguously.

In addition to the problems associated with assigning specific bands to ethers, there is a problem in measuring OH groups using the standard KBr preparation method. Friedal (9) discussed in some detail the difficulty in removing water absorbed on the KBr discs during sample preparation and noted that heating to 175°C is required to completely remove water bands, which nevertheless reappear upon cooling. Consequently, in order to determine changes in hydroxyl and ether groups upon oxidation we decided to combine FTIR with chemical methods of analysis. Samples were acetylated in order to determine hydroxyl groups and reacted with potassium in THF, as described by Wachowska, et al. (5), in order to cleave ether bonds.

Durig and Sternhell (9) reported an infrared study of acetylated coal twenty years ago. Although some useful linear plots were obtained, the method was complicated by the overlap of the acetyl bands with those of the original coal. This made the determination of baselines and the measurement of peak intensities (and hence reactive OH groups) subject to possible error. The problem is illustrated in Figure 2, which compares the infrared spectrum of an Arizona HVC coal (PSOC 312) to that of the same sample subsequent to acetylation. FTIR is capable of solving many problems of this type (band overlap) by simple spectral subtraction. Figure 2 also shows the difference spectrum obtained by subtracting the spectrum of the original coal from that of the acetylated product. The characteristic acetyl bands are now relatively well-resolved and it is a straight-forward task to draw an appropriate baseline and measure peak heights, or even make integrated absorption measurements of, for example the 1370 CH_3 mode. We have 'calibrated' the intensities of these bands, so that we can obtain a measure of the number of reactive OH groups, but this work will be reported elsewhere. In this study our initial aim was to determine qualitatively the change in OH content upon oxidation. Figure 3 compares the infrared spectrum of acetylated fresh PSOC 337 coal to the spectrum of the acetylated oxidized (150°C , 2 hours in air) coal. Difference spectra of the type shown in Figure 2 were obtained and intensity measurements of the acetyl bands indicated a reduction in the number of reactive OH groups under these conditions of oxidation. This reduction can be seen in Figure 3, which also shows two difference spectra (acetylated oxidized - acetylated fresh sample). Two different subtraction criteria were used, first the elimination of the coal 1600 cm^{-1} band and second the subtraction to the baseline of the aliphatic CH bands near 2900 cm^{-1} . In both difference spectra there are negative bands characteristic of the acetyl group, near 1770 , 1370 and 1200 cm^{-1} , indicating a loss of reactive OH group content upon oxidation. At this time we are not convinced that this reduction in the number of OH groups is a direct consequence of oxidation. At elevated temperatures there is also the possibility of condensation reactions between phenolic OH groups. We are still in the process of investigating this point thru the study of coals oxidized at lower temperatures.

As we noted above, in a number of studies it has been concluded that the formation of ether cross links are critical to loss of coking ability. For example, it has been observed that the swelling behavior of coking coal can be

partially regenerated by treating with potassium in THF, a reagent that should cleave C-O bonds but not C-C bonds (5). We therefore considered it valuable to apply FT-IR to the characterization of the chemical changes occurring upon reaction of potassium in THF with oxidized coal. The spectrum of an oxidized coal (3.3% oxygen uptake) is compared to the spectrum of the same sample treated with potassium in THF in Figure 4. We were surprised by the observation that this treatment apparently leads to an increase in the degree of oxidation of the sample, as measured by the increased intensity of the shoulder near 1695 cm^{-1} . This is confirmed by the difference spectrum, shown in the same figure, which is remarkably similar to the difference spectrum shown in Figure 1. The criteria for obtaining this difference spectrum differs from that used previously, in that, because kaolinite is lost from the sample during the course of the reaction, it is no longer a suitable subtraction standard. Instead, we subtracted the aliphatic C-H modes near 2900 cm^{-1} to the baseline. Because of the weak intensity of this band, this subtraction is only approximate. Nevertheless, the carboxyl band, now appearing near 1580 cm^{-1} , is again revealed.

We postulated that the increased oxidation of the sample might occur in the final stage of the reaction procedure, where the coal is dried at 70°C (7,8). Consequently, we modified the procedure so that the final product was dried under vacuum at room temperature. The results remained the same. For example, the spectrum of the unoxidized coal is compared in Figure 5 to the spectrum of the same sample after reaction. Again a carbonyl band appears as a shoulder near 1695 cm^{-1} . However, there is also an apparent decrease in intensity of the band near 1265 cm^{-1} (which was not observed in the spectra of samples dried at 70°C ; see Figure 4), suggesting that some C-O bonds are being cleaved. The reaction of coal with potassium in THF therefore appears more complex than considered in previous studies and does not lead to cleavage of C-O bonds alone. It is important to note that Wachowska, et al. (5) detected an increase in oxygen content of both fresh and oxidized coal upon reaction, an increase that manifests itself in our study as an increase in carbonyl and carboxylic acid groups.

Finally, we were surprised by the observation that in our oxidized samples⁻¹ the carboxylic acid groups are in the salt form, thus giving bands near 1575 cm^{-1} one possibility is that there has been an exchange with potassium ions in the KBr matrix used for sample preparation. Alternatively, $-\text{COO}^-$ groups have a counterion (e.g. Ca^{++}) derived from the mineral matter. Miller (10,11) has reported that in the low temperature ashing process used in mineralogical analysis organic sulfur is fixed as inorganic sulfate in the form of bassanite, but only if there are carbonate or $-\text{COO}^-$ groups present. If the carboxyl groups are converted to the acid form, $-\text{COOH}$, then organic sulfur is no longer fixed. We have observed similar results in FTIR studies (12,13) and also observed a corresponding fixation of organic nitrogen as inorganic nitrate. If we examine the infrared spectra of the low-temperature ash of a coking coal samples as a function of degree of oxidation (6) we can see bands characteristic of bassanite (near 605 and 660 cm^{-1}) and nitrate (1386 cm^{-1}) in the spectra of oxidized samples which are absent or extremely weak in the spectra of the ash of unoxidized samples, as illustrated in Figure 6. Previously, Pearson and Kwong (14) have noted an empirical correlation of bassanite concentration with the degree of oxidation of a coking coal. This can now be explained by the presence of $-\text{COO}^-$ groups in these coals which allow the fixation of organic sulfur as inorganic sulfate. These results also demonstrate that in the oxidized coals used in this study carboxyl groups are present in the salt form, presumably through interaction with the mineral matter present in the coal.

CONCLUSIONS

In the early stages of coal oxidation the principal products appear to be carbonyl and carboxyl groups. Oxidation at 150°C appears to result in a slight loss of phenolic OH, possibly through condensation reactions to give ethers.

REFERENCES

1. Ignasiak, B. S., Clugston, D. M. and Montgomery, D. S. Fuel 51, 76 (1972).
2. Carbonization Research Report 64, February 1979. The British Carbonization Research Association, Chesterfield, Derbyshire, England.
3. Wachowska, H. and Angelova, G. Fuel, 56, 422 (1977).
4. Ignasiak, B. S., Nandi, B. N. and Montgomery, D. W. Fuel, 49, 214 (1970).
5. Wachowska, H. M., Nandi, B. N. and Montgomery, D. S. Fuel, 53, 212 (1974).
6. Painter, P. C., Snyder, R. W., Pearson, D. E. and Kwong, J. Fuel, 59, 282 (1980).
7. Painter, P. C. and Snyder, R. W. ACS Division of Fuel Chemistry preprints (1980).
8. Painter, P. C., Coleman, M. M., Snyder, R. W., Mahajan, O., Komatsu, M. and Walker, P. L., Jr. Applied Spectroscopy (In press).
9. Friedel, R. A. in Applied Infrared Spectroscopy, p. 312. Edited by Kendall, D. N. Reinhold, New York (1966).
10. Miller, R. N. Ph.D. Thesis, 1977, The Pennsylvania State University.
11. Miller, R. N., Yarzab, R. F. and Given, P. H. Fuel, 58, 4 (1979).
12. Painter, P. C., Coleman, M. M., Jenkins, R. G. and Walker, P. L. Jr. Fuel, 57, 125 (1978).
13. Painter, P. C., Youtcheff, J. and Given, P. H. Fuel 59, 523 (1980).
14. Pearson, D. E. and Kwong, J. Fuel, 58, 63 (1979).

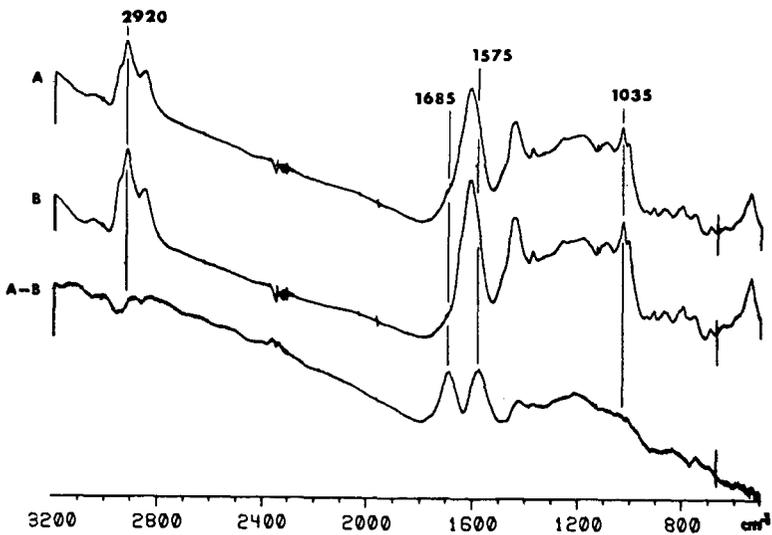


Figure 1: A: FTIR spectrum of coal (PSOC 337) oxidized at 150°C for 2 hours.
 B: FTIR spectrum of the original coal (PSOC 337).
 A-B: Difference spectrum.

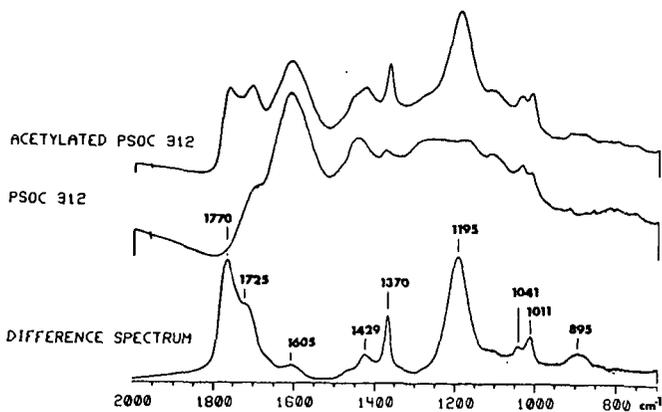


Figure 2: Top: FTIR spectrum of an acetylated Arizona coal (PSOC 312).
 Middle: FTIR spectrum of the original coal (PSOC 312).
 Bottom: Difference spectrum.

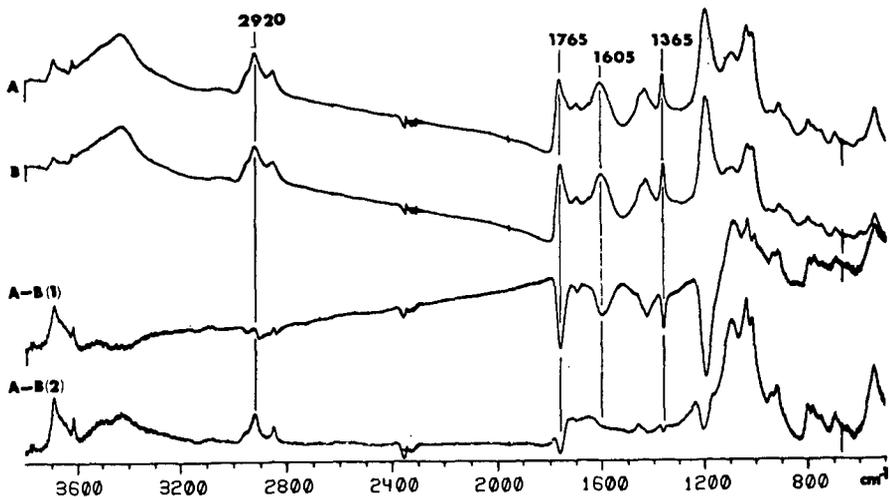


Figure 3: A: FTIR spectrum of acetylated coal (PSOC 337) oxidized at 150°C for 2 hours.
 B: FTIR spectrum of acetylated, fresh coal (PSOC 337).
 A-B: (1) Difference spectrum subtracting 2920 band to the baseline.
 A-B: (2) Difference spectrum subtraction 1605 band to the baseline.

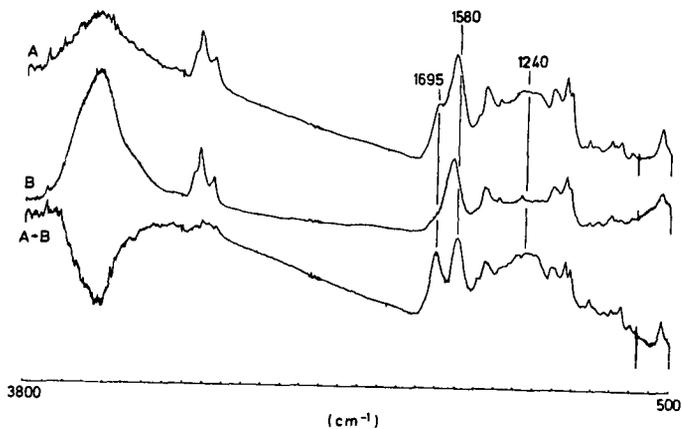


Figure 4: A: FTIR spectrum of oxidized coal after treatment with potassium in THF.
 B: FTIR spectrum of oxidized coal.
 A-B: Difference spectrum.

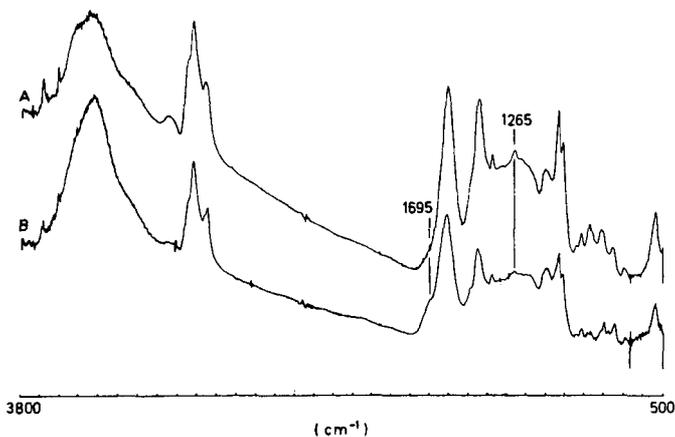


Figure 5: A: FTIR spectrum of fresh, unoxidized coal.
 B: FTIR spectrum of unoxidized coal after treatment with potassium in THF.

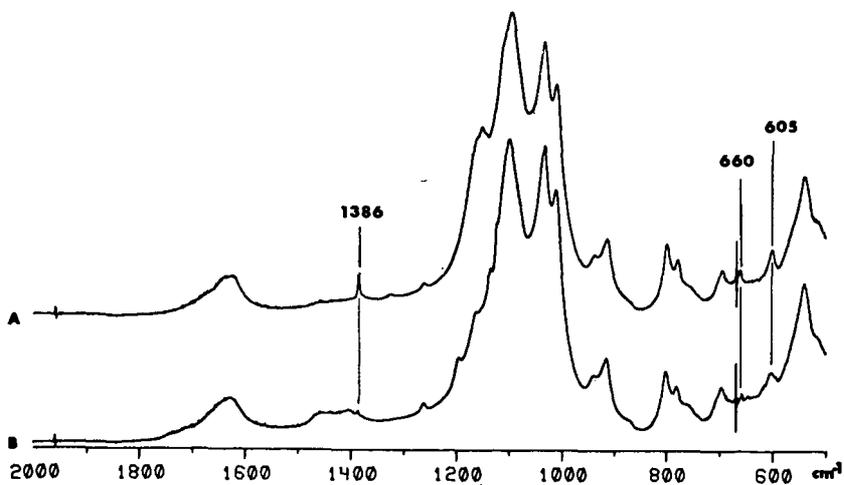


Figure 6: A: FTIR spectrum of low temperature ash (LTA) from highly weathered Canadian coking coal.
 B: FTIR spectrum of low temperature ash (LTA) from a less weathered Canadian coking coal.

THIN SECTION MICROSCOPIC STUDIES OF THE
DIFFUSION OF OXYGEN INTO COAL AT ELEVATED TEMPERATURES

D. Brenner

Corporate Research Science Laboratories
Exxon Research and Engineering Company
P.O. Box 45, Linden, N. J. 07036

Introduction

The oxidation of coal is important to a range of coal technologies. These include oxidation of lignites in storage piles, which can cause spontaneous combustion, the detrimental effect of oxidation on liquid yields in liquefaction and on the coking properties of metallurgical coal, and the use of oxidation to inhibit the swelling of coal in both liquefaction and gasification processes. Optical microscopy has been an important means of investigating oxidation in coal for many years. Such studies generally involve the observation of polished surfaces of coal using reflected light. Immersion oil is also normally used to increase the contrast between the various components of the coal. A number of studies of coal oxidation using reflectance microscopy have been reported. Peters and Jüntgen (1) observed oxidation borders around particles of coal exposed to oxygen at 230°C. They also developed mathematical equations to describe the rate of widening of these oxidation borders from the surface towards the center of a coal particle. Other reflectance studies on oxidized or weathered coals have been reported by Chandra (2), Benedict and Berry (3) and Goodarzi and Murchison (4).

Transmitted light optical microscopy employing thin section samples is also used in the study of coal. Because of the high light absorption of coal, these samples must be less than about 20 micrometers thick. Thin section microscopy of coal was common some 40 years ago. In particular, Thiessen (5) and other workers at the U.S. Bureau of Mines used this technique extensively. However, although some workers continue to use thin section techniques to study coal, since the 1950's reflected light microscopy of coal using polished surfaces and immersion oil has become predominant. Reasons for this include ease of preparation of the samples and the ability to readily obtain quantitative data from measurements of the reflectivity of the coal surface. There are a few references to the use of thin sections for the study of thermally metamorphized coals, such as the work by Marshall (6), but no references to the use of transmitted light microscopy for the study of coals oxidized at elevated temperatures have been found. In the present study it was discovered that transmitted light microscopy using thin section samples of coal was far more sensitive to the effects of oxidation than the conventional reflected light microscopy of coal. In the present investigation thin section samples are utilized to study the pathways for rapid penetration of oxygen into coal.

Experimental

Illinois #6 coal was ground and sieved to obtain a 20 X 30 U.S. mesh cut. This sample was washed of fines in distilled water and then dried overnight in vacuum at 120°C. It was then stored in nitrogen at room temperature. The samples were oxidized at atmospheric pressure in a Perkin-Elmer TGS-2 thermogravimetric analyzer. The gas consisted of 1 mole per cent oxygen in argon. The samples described in this study were heated at 160°C per minute to 365°C and held at that temperature for 15 minutes unless otherwise noted. They were then cooled rapidly.

The oxidized coal particles were embedded in epoxy, and thin section samples were prepared using procedures similar to those described by Ting (7). A Leitz Ortholux II-Pol BK microscope was used for observing the samples and a Wild photo-automat MPS 50 automatic 35mm camera system was used for taking photomicrographs with Kodak High Speed Ektachrome ASA 400 daylight film. The color slides were converted to black and white prints for this paper.

Results and Discussion

A part of a thin section of an oxidized coal particle is shown in the transmitted light photomicrograph of Figure 1. This specimen, of relatively uniform vitrinite, has a thin oxidation border around its periphery. The border, which is about four micrometers thick, is unusually uniform; this is indicative of the homogeneity of this particular piece of coal. The narrowness of the border shows that the diffusion of the oxygen into the homogeneous vitrinite is quite slow.

An internal region of a sample of vitrinite, which was oxidized at 365°C for three minutes, is shown in Figure 2. The sample is permeated by a number of cracks and holes. The dark areas bordering these regions are oxidized. This shows that cracks and holes are pathways for rapid penetration of oxygen into the coal structure. Around some of these regions the oxidation borders are thin, much as they were at the surface of the particle in Figure 1. However, around most of the holes and cracks there are massive blackened areas. In these regions the vitrinite has become microporous permitting rapid penetration by the oxygen.

The darkened oxidation regions in these coal particles are not a consequence of localized heating of the coal or pyrolysis. There are several reasons why localized heating would not be a problem:

- (a) The oxygen concentration in the surrounding gas is quite low, only 1.0 mole per cent,
- (b) Oxidation occurs along deep cracks and at other spots deep within the coal, as well as at the surface. This indicates that the oxidation is not appreciably enhanced by temperature gradients from the surface to the interior of the particles,
- (c) Many of the oxidation borders are quite narrow, so the temperature gradients across them must be quite small,
- (d) When this coal is heated in the absence of oxygen to more than 20°C higher than the temperatures used in this experiment, no blackening effects such as those caused here by oxidation are observed,
- (e) The temperature of the coal in this experiment was carefully controlled and the sample size was only about 20 mg,
- (f) Finally, similar darkening effects due to oxidation were observed in coal which was oxidized at temperatures as low as 150°C.

In Figure 3 exactly the same region of the same particle as was shown in Figure 2 is again shown, except this time it is viewed in reflected light using immersion oil. Many of the oxidized areas are not readily evident. This shows that transmitted light microscopy of thin sections is a far more sensitive technique for studying the effects of oxidation of coal at elevated temperatures than is reflectance microscopy.

A section of coal containing a circular maceral is shown in Figure 4. This maceral, which is classified as a "resin rodlet" is a type of vitrinite. Resin rodlets appear to quite homogeneous and they apparently have very little porosity. This is illustrated in Figure 4 where almost the whole interface between the resin rodlet and the common type of vitrinite is darkened by oxidation; but although the oxidation extends well into the common vitrinite material, there is almost no penetration of the resin rodlet.

The overall sample in Figure 4 is somewhat heterogeneous as can be seen from the variations in the lightness of the material (apart from oxidation). This heterogeneity is probably the reason for the rather high degree of penetration of oxygen

into this particle (the blackened regions) both in interior regions and at the surface (for example, compare this particle with the one in Figure 1). Note that some parts of the surface of this particle have a very narrow oxidation border--such as just below the large crack--whereas around most of the surface there is substantial penetration. These variations are indicative of the heterogeneity of this particle. Also, note that the oxidation border along the large crack is narrow from its mouth up to about half way along its length, but the end region of the crack has a massive oxidized area around it. Large oxidized areas around the ends of cracks are quite common; they are probably a result of the fracture mechanism (or the termination of fracture propagation) in the coal. It is likely that a multitude of microfractures are formed at the tip of the propagating crack due to the stresses created in the fracture process. These microfractures broaden the region of stress concentration around the crack tip and thereby terminate crack propagation.

A sample of coal containing a considerable amount of liptinite material is shown in Figure 5. The liptinite is the lighter bands in the photomicrograph. Some of the liptinite is derived from spore walls and possibly some of it is resinous material. It is clear from this photomicrograph that the oxygen only penetrates the liptinite regions slowly (in the absence of cracks). The penetration appears to be no faster than for the adjacent vitrinite regions. Even where oxygen penetrated across one of the liptinite macerals at the top of the photomicrograph (probably along a crack), the further diffusion of oxygen into the maceral was slow. There is no indication of oxygen penetration at the interface between the liptinite and vitrinite bands. This indicates very intimate bonding between these macerals. However, there does appear to be penetration of oxygen (darkened diffuse lines) at the interfaces between some rectangular vitrinite macerals in the left-middle part of the figure and the larger bands of vitrinite in which they are contained.

Only a small fraction of the pieces of coal observed in this study at 365°C showed the formation of vacuoles (i.e. swelling). Figure 6 is a photomicrograph of one of the pieces containing a vacuole. The particle has a thin border of oxidized material at the surface but there is no trace of oxidation on the interior border of the vacuole. This indicates that either there were no sizable pathways to the surface of the coal particle, or if there were such pathways, gases escaping from the vacuole prevented significant counter diffusion of oxygen. With respect to this latter possibility, it should be noted that cracks in the coal which have an opening on the surface invariably have an oxidation border in spite of any gases being released from the coal--this even includes very long and very narrow microcracks. On the other hand, a vacuole has far more surface area to take up any oxygen which enters it than does a crack. It is interesting that in spite of the large vacuole in this particle, no distortion of the surface of the particle is evident. This suggests that the oxidation rim has a strong reinforcing and stabilizing effect on the surface of the particle.

A heterogeneous region of vitrinite material is shown in Figure 7. On the left side of this photomicrograph are some resin rodlets embedded in striated (thin bands) vitrinite. In this disrupted region of the coal, substantial penetration of oxygen (the black areas) is found. The oxidation tends to follow along the striations indicating poor contact or bonding at the interfaces between the different macerals. However, in many particles which have a relatively regular banding pattern, penetration of the coal structure has been observed to be slight.

A sample of relatively homogeneous vitrinite with several pieces of pyrite embedded in it is shown in Figure 8. This photomicrograph utilized a combination of transmitted light and reflected light on a thin section sample. The light spots in the coal are the pyrite, the diffuse dark regions are the oxidized areas. In transmitted light alone the pyrite would be black, so the pyrite could be distinguished from an oxidized region only by its shape or by its sharp border (as contrasted with the diffuse borders of oxidized regions). In Figure 8, however, the area around the pyrite has been oxidized so use of reflected light was necessary in order to see the interface between the pyrite and the oxidized regions of the vitrinite. In samples that contained particles of pyrite it was often found that the area around the pyrite was oxidized such as was seen in Figure 8--especially if the pyrite was near the surface of the particle. Apparently the interface between the pyrite and the vitrinite

is porous or perhaps the particles of pyrite have porous structures.

In addition to the studies of oxidation described above using an exposure temperature of 365°C, observations were made recently on samples oxidized at temperature as low as 150°C. Even at 150°C oxidized regions of the coal were readily observable in thin section samples as darkened areas. These results are in contrast to reflectance studies of coal oxidation where oxidation rims have not been observed for exposure temperatures below 170°C and where detection of oxidation is extremely difficult even for an exposure temperature of 200°C (8).

Conclusions

Transmitted light optical microscopy using thin section samples has been found to be substantially more sensitive to regions of coal oxidized at elevated temperatures than conventional reflected light coal microscopy. This higher sensitivity enables detection of mild oxidation which would go undetected in reflectance observations. It also allows study of the locations of oxidation in greater detail than is possible with reflectance microscopy. It was found that major pathways for rapid penetration of oxygen into coal particles included maceral interfaces, heterogeneous or disrupted microstructures, and mineral matter, as well as cracks and holes. Penetration of oxygen into coal was slow in homogeneous vitrinite and in the observed liptinite macerals. Penetration was particularly slow in resin rodlets. The pathways for penetration of coal by oxygen are probably also relevant to the penetration of coal by other gases, vapors, and even liquids.

Acknowledgements

The author acknowledges the excellent technical assistance of Mark S. Beam in carrying out the oxidation treatments and the preparation of samples.

References

1. Peters, Von W., and Jüntgen, H., Brennstoff-Chemie 46(2), 56 (1964).
2. Chandra, D., Econ. Geol., 53, 102-108 (1958).
3. Benedict, L. G., and Berry, W. F., Coal Sci., Adv. Chem. Ser. 55, 577-601 (1966). Published by Am. Chem. Soc., Washington, D. C. (1966).
4. Goodarzi, F., and Murchison, D. G., Fuel, 52, 164, (1973).
5. Thiessen, R., U.S. Bur. of Mines Tech. Paper 564 (1935).
6. Marshall, C. E., Fuel, 24, 120, (1945).
7. Ting, F. T. C., Analytical Methods for Coal and Coal Products, edited by C. Karr Jr., Volume I, Chpt. 1, (1978). Published by Academic Press, New York.
8. Chandra, D., Stach's Textbook of Coal Petrology, 164, (1975). Published by Gebrüder Borntraeger, Berlin, 1975.

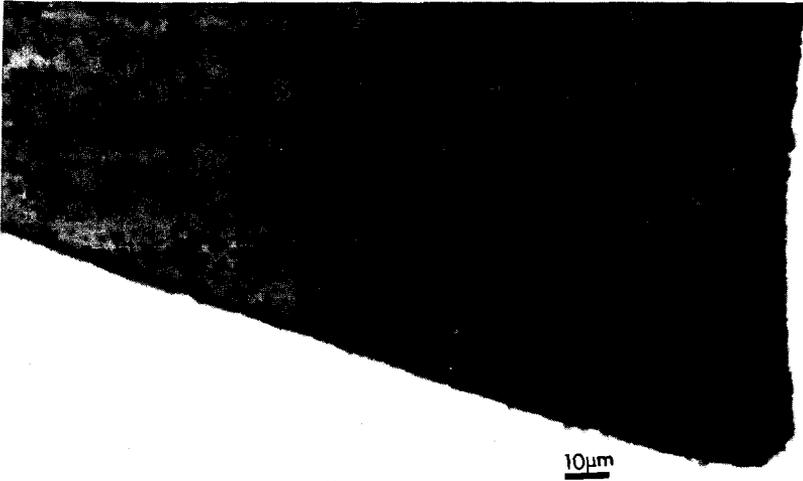


Fig. 1. Thin oxidation border around relatively homogeneous vitrinite



Fig. 2. Internal oxidation around cracks and holes and in micro-fissured regions

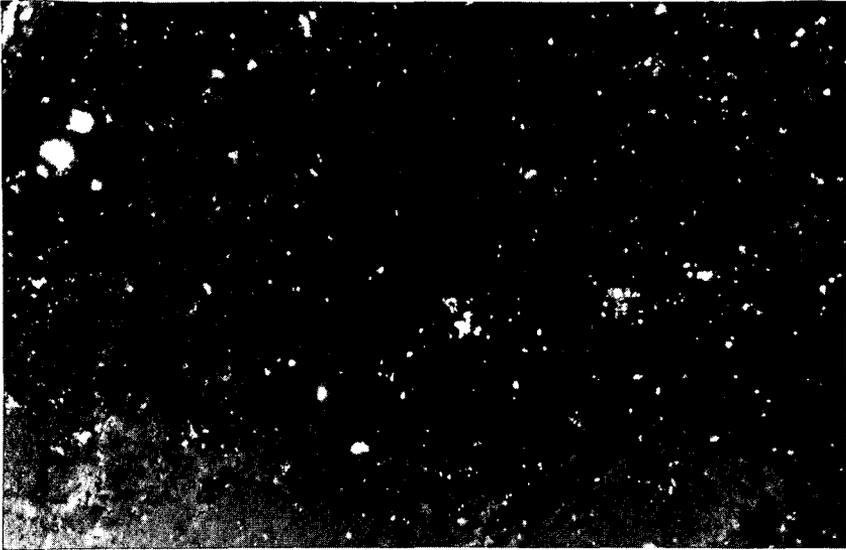


Fig. 3. Reflected light illumination using immersion oil of same area as was shown in Fig. 2

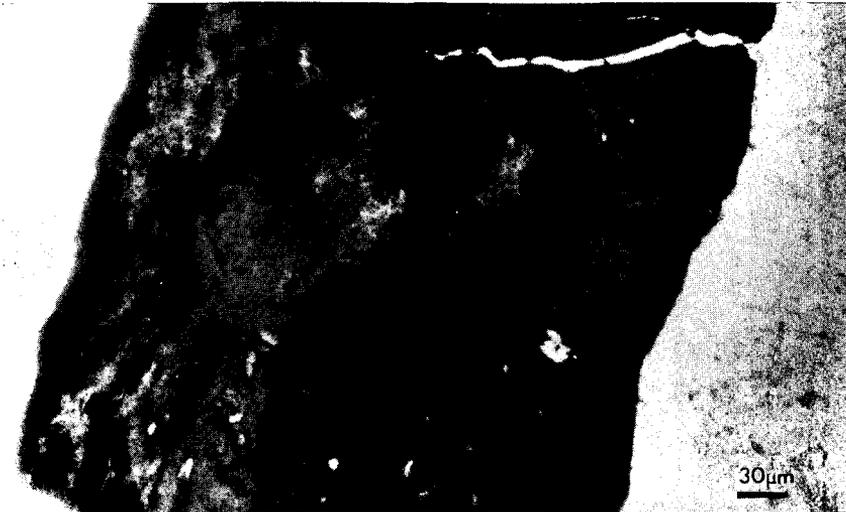


Fig. 4. Oxidation at a maceral interface, but with very little penetration of a resin rodlet

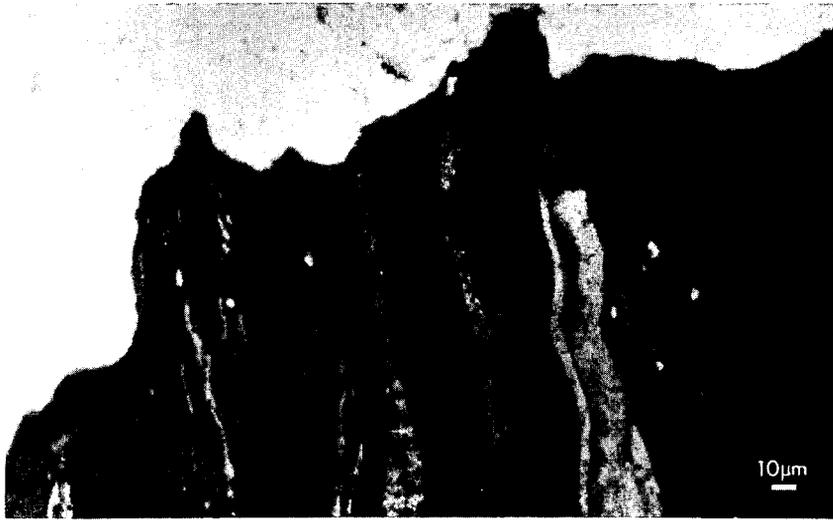


Fig. 5. Slow oxygen penetration into liptinite macerals with no observed penetration along the liptinite-vitrinite interface



Fig. 6. Vacuole with no oxidation along its interior surface

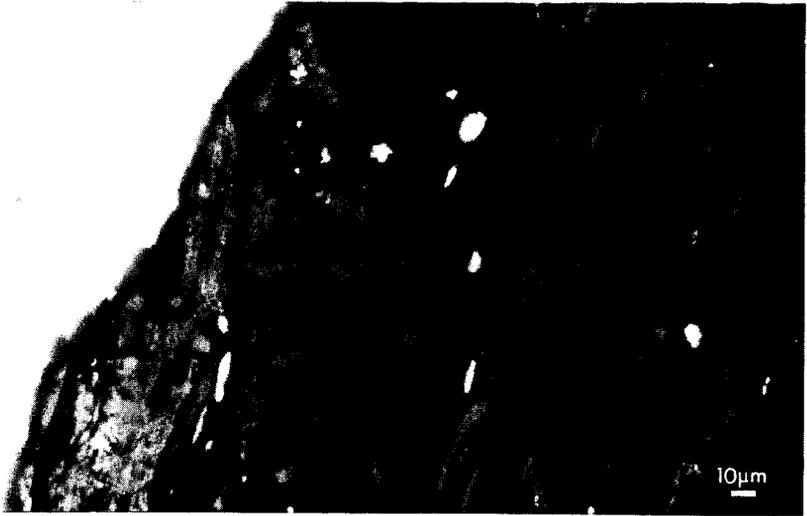


Fig. 7. Extensive oxidation in heterogeneous regions in a particle of coal



Fig. 8. Oxidation around pyrite granules as observed in combined transmitted and reflected light

CHEMICAL STUDIES OF THE AMES OXYDESULFURIZATION PROCESS

Thomas G. Squires, Clifford G. Venier, Lawrence W. Chang, and Thomas E. Schmidt

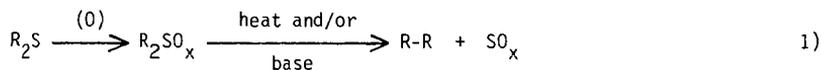
Ames Laboratory*, Iowa State University, Ames, Iowa 50011

In freshly mined coal, sulfur is present in two major forms: as iron pyrite and as organic sulfur, i.e., as sulfur chemically bonded to carbon and thus comprising an integral part of the organic coal matrix(1). The pyritic sulfur is distributed in varying proportions between large framboidal pyrite, the major portion, and microfine pyrite which is encapsulated in the organic coal matrix. While the majority of the pyrite can usually be removed by conventional physical beneficiation processes, encapsulated microfine pyrite as well as organic sulfur are not responsive to these cleaning procedures. Consequently, a number of chemical oxydesulfurization procedures have been proposed and investigated in order to supplement the physical beneficiation of coal. One of these techniques, the Ames Process(2), utilizes 0.2 M aqueous Na_2CO_3 at 150°C under a pressure of 200 psi O_2 for one hour.

Some of the early model compound work on the Ames Process was done by Greer and Wheelock(3). These workers investigated the effect of the Ames Process on iron pyrite and were able to demonstrate quite dramatically that pyrite (FeS_2) is converted to hematite (Fe_2O_3) under the process conditions.

The assessment of the efficacy of the Ames Process in removing organic sulfur from coal is much more complicated due to the inaccuracy of the ASTM method for determining organic sulfur in coal and the paucity of information detailing the organic sulfur functional group distribution in coal. The inaccuracy of the quantitative method for determining organic sulfur can be attributed partially to a lack of precision in the ASTM method of determining organic sulfur by difference, which Paris(4) has found to be as high as $\pm 25\%$ at two standard deviations. An additional source of error has been shown by Greer(5) to involve organically encapsulated microfine pyrite. While this pyrite would be inert to extraction with nitric acid in the raw coal and thus would report as organic sulfur, subjecting the coal to $150\text{--}200^\circ\text{C}$ for an hour in the presence of water and oxygen should remove this microfine pyrite or, at least, render it accessible to the nitric acid extraction. The data generated from the treated coal would indicate an apparent removal of organic sulfur. On the basis of these considerations, the evaluation of organic sulfur removal by the ASTM method could easily be in error by as much as $\pm 50\%$ of the raw coal value. Since both the PETC and Ames Oxydesulfurization Processes claim the removal of organic sulfur from coal up to a maximum of 40%, we set out to assess the validity of these claims by subjecting model compounds to the Ames conditions.

Conceptually, this type of oxydesulfurization has been described as a two step process involving initial oxidation at sulfur to produce sulfoxides and sulfones. This step is then though to be followed by the thermal and, in the Ames Process,

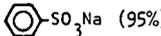
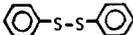
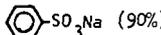
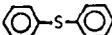
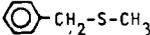
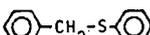


base assisted extrusion of SO_x . In this formulation, the initial oxidation at sulfur facilitates desulfurization by polarizing and weakening the carbon to sulfur bond(6).

*Operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

The results for model compounds are presented in Table 1. The lack of reactivity exhibited was surprising. In order to assess the possibility that coal may act as a catalyst in the oxidation, reactions of several compounds were carried out in the presence of coal. These results are shown in Table 2.

TABLE 1. EFFECT OF AMES PROCESS ON MODEL ORGANIC SULFUR COMPOUNDS^a

MODEL COMPOUND	RECOVERED STARTING MATERIAL	YIELDS	
		PRODUCTS	
	0%	 (95%)	
	5%	 (90%)	
	96%	No reaction	
	87%	No reaction	
	98%	No reaction	
$(n-C_8H_{17})_2S$	90%	No reaction	
	36%	 (23%),  (34%), CH_3SO_3Na (55%)	
	29%	 (31%),  (18%),  (51%)	

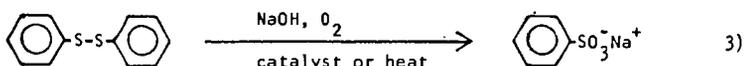
^a150°C, 200 psi O₂, 0.2M aqueous Na₂CO₃, 1 hour.

TABLE 2. EVALUATION OF POSSIBLE COAL CATALYSIS IN AMES PROCESS

Model Compound	Yield of Recovered Starting Material		
	Model Compound Alone	Lovilia Coal Added	
		N ₂	O ₂
Dibenzothiophene	96%	83%	76%
Diphenyl Sulfide	98	76	74
Diocetyl Sulfide	90	--	82
Benzyl Methyl Sulfide	36	75	13

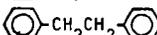
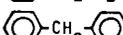
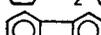
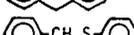
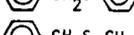
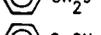
In order to take into account the decreased recovery expected due to adsorption of the model compounds onto coal, runs using both oxygen and nitrogen were performed. The results confirm that simple sulfides and dibenzothiophene, the principle functional groups expected to be in coal, are inert to oxidation under the Ames Process conditions.

Of the reactive functions, thiophenols are widely known to undergo facile air oxidation to disulfides (7) and the oxidation of thiophenols and disulfides to sulfonic acids under more forcing conditions is also known(8). That leaves the results of the reaction of two compounds, benzyl methyl sulfide and benzyl phenyl



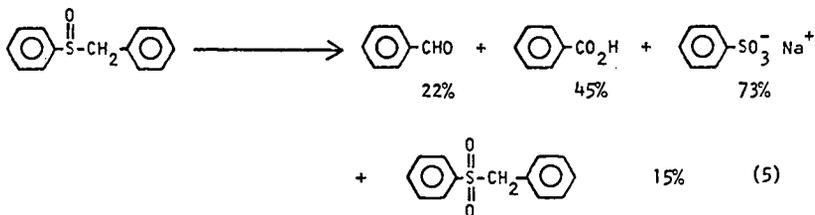
sulfide, to be explained. The fact that it is only the benzylic sulfides which are reactive is reminiscent of hydrocarbon autoxidation, a long known and well studied process which involves the free radical abstraction of hydrogen from weak carbon-hydrogen bonds(9). Table 3 presents the relative rates of hydrogen abstraction from some representative compounds by phenyl radical(10), the most studied of the hydrogen abstractors and t-butylperoxy radical(11), more closely similar to the peroxy radicals which we postulate would be the hydrogen abstracting species in the Ames Process, as well as the autoxidation rate of the pure compounds.

TABLE 3. RELATIVE RATES OF HYDROGEN ABSTRACTION BY FREE RADICALS

Compound	Ph·, 60°C ^a	(CH ₃) ₃ COO·, 30°C ^b	RH + ROO·, 30°C ^b
	(1.0)	(1.0)	(1.0)
	3.6	5.0	2.3
	5.1	8.9	8.3
	13.	---	---
	17.	4.4	40.
	8.2	---	---
	1.4	---	---

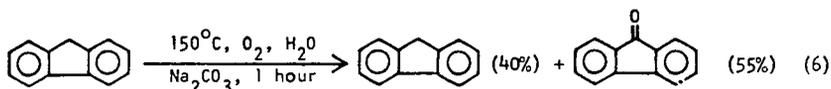
^aData of reference 10. ^bData of reference 11.

In order to rule out the possibility that the benzylic sulfides are in fact oxidized to either the sulfoxide or sulfone, which then are responsible for the observed products, both benzyl phenyl sulfoxide and benzyl phenyl sulfone were subjected to the reaction conditions. Because the sulfone is inert, it can be ruled out as a possible reaction intermediate. Although it does react, the sulfoxide gives sulfone as one of the products. Since sulfone is not isolated in the oxidation of sulfide under process conditions, the sulfoxide is also eliminated as a



possible reaction intermediate.

Beside benzylic sulfides, one would expect that some hydrocarbons, for example, fluorene, would also be reactive to the oxydesulfurization conditions. Under Ames process conditions, fluorene is indeed degraded to its known autoxidation product, fluorenone(13). While we have not yet run other hydrocarbons which might be expected to be reactive, we believe that they will behave similarly.



Fledgling studies of sulfur-containing synthetic polymers(14) add support to the model compound studies. Table 4 shows the results of subjecting three modified polystyrenes to the Ames Process conditions. Both the phenylthiomethyl and tolylthiomethyl polystyrenes are analogs of the model compound, benzyl phenyl sulfide. As we had anticipated, the solid polymers, which should be better models for solid coal, were reactive, but less so than the corresponding model compound. Polystyrene cross-linked by dibenzothiophene is unreactive, confirming the inertness of the dibenzothiophene moiety to oxydesulfurization.

TABLE 4. EFFECT OF THE AMES PROCESS ON SULFUR-CONTAINING POLYSTYRENE POLYMERS^a

Polymer ^b	%Sulfur Removed
$\text{P-CH}_2\text{-S-C}_6\text{H}_5$	10%
$\text{P-CH}_2\text{-S-C}_6\text{H}_4\text{-CH}_3$	20%
$\text{P-CH}_2\text{-DBT-CH}_2\text{-P}$	0

^a150°C, 200 psi O₂, 0.2 M aqueous Na₂CO₃, 1 hour.

^b P = polystyrene backbone; substituents are attached through the para position.

DBT = dibenzothiophene nucleus,

Finally, we have subjected the pyridine extract of an Illinois #6 coal to the Ames Process conditions. All of the sulfur in an extract is organically bound and hence, the quite accurate total sulfur determination is also the organic sulfur determination. The results in Table 5 show that oxydesulfurization apparently does not reduce the organic sulfur level of the extract. On the other hand, some of the extract is apparently oxidized as judged by the increase in S/C ratio, the increase in oxygen content, and the increased O/C ratio.

Our conclusions concerning the oxydesulfurization process as gleaned from model compound studies are, in summary, the following:

1. Thiophenols and disulfides are the only groups oxidized at sulfur.
2. Sulfides, including thiophenes, are not oxidized at sulfur.
3. Reactive sulfides are oxidized at reactive carbon-hydrogen bonds.
4. Reactive carbon-hydrogen bonds in functions not containing sulfur also react.
5. The Ames Process is directly analogous to hydrocarbon autoxidation.
6. More efficient sulfur removal without severe degradation of the coal is not possible under the present process conditions.

The success which these model compound studies have had in defining the limits of the efficacy of the Ames oxydesulfurization process encourage us to believe that this approach will be quite valuable in the evaluation of other proposed chemical coal cleaning techniques.

Table 5. EFFECT OF AMES PROCESS ON PYRIDINE EXTRACT OF ILLINOIS #6 COAL^a

Datum	Extract	Ames Processed Extract	
		N ₂ ^b	O ₂ ^c
Weight recovered	--	93%	85%
Elemental Analysis ^d			
C	76.6	77.9	68.5
H	6.1	5.8	4.9
S	0.8	0.8	0.9
O (by diff.)	14.4	12.8	22.3
S/C ratio (moles)	0.028	0.026	0.034
H/C ratio (moles)	0.95	0.90	0.85
O/C ratio (moles)	0.25	0.22	0.43

^a150°C, 0.2 M aqueous Na₂CO₃, 1 hour. ^b200 psi N₂ pressure. ^c200 psi O₂ pressure.

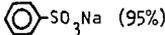
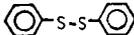
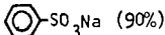
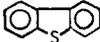
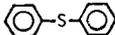
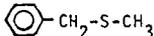
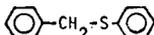
^dSamples contain a small amount of ash or NaCl. Element percents are expressed ash or NaCl free.

REFERENCES

1. (a) R. M. Davidson, Molecular Structure of Coal, IEA Coal Research Report No. ICTIS/TR 08, London, 1980; (b) D. D. Whitehurst, in Organic Chemistry of Coal, J. W. Larsen, ed., A. C. S. Symposium Series, 71, 1-35 (1978).
2. C. Y. Tai, G. V. Graves, and T. D. Wheelock, in Coal Desulfurization, T. D. Wheelock, ed., A. C. S. Symposium Series, 64, 182-197 (1977).
3. T. D. Wheelock, R. T. Greer, R. Markuszewski, and R. W. Fisher, Advanced Development of Fine Coal Desulfurization and Recovery Technology, Annual Technical Progress Report, Oct. 1, 1976 - Sept. 30, 1977, submitted to the U. S. Department of Energy, Ames Laboratory, Iowa State University, Document No. IS-4363, March, 1978.
4. B. Paris, in Coal Desulfurization, T. D. Wheelock, ed., A. C. S. Symposium Series, 64, 22-31 (1977).
5. R. T. Greer, in O. Johari, ed., Scanning Electron Microscopy/1978, Vol. 1, SEM, Inc, Chicago, 1978, pp. 610, 621-6.
6. A. Attar and W. H. Corcoran, Ind. Eng. Chem., Prod. Res. Dev., 17, 102 (1978).
7. A. Ohno and S. Oae, in Organic Chemistry of Sulfur, S. Oae, ed., Plenum Press, New York, NY, 1977, Chapter 4, pp. 119-187.
8. H. Berger, Rec. trav. chim. Pays-Bas, 82, 773 (1963).
9. J. A. Howard, in Free Radicals, J. K. Kochi, ed., Vol. 11, Wiley-Interscience, New York, NY, 1973, Chapter 12, pp. 3-62.
10. G. A. Russell, in Free Radicals, J. K. Kochi, ed., Vol. 1, Wiley-Interscience, New York, NY, 1973, Chapter 7, pp. 275-331.
11. D. G. Hendry, T. Mill, L. Piskiewicz, J. A. Howard, and H. K. Eigenmann, J. Chem. Phys. Ref. Data, 3, 937-78 (1974).
12. J. G. Huntington, F. R. Mayo, N. A. Kirshen, Fuel, 58, 31-36 (1979).
13. G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geets, A. J. Moye, S. Mak, and E. T. Strom, Adv. Chem. Series, 51, 112-171 (1964).
14. The details of synthesis will be published in another place.

The results for model compounds are presented in Table 1. The lack of reactivity exhibited was surprising. In order to assess the possibility that coal may act as a catalyst in the oxidation, reactions of several compounds were carried out in the presence of coal. These results are shown in Table 2.

TABLE 1. EFFECT OF AMES PROCESS ON MODEL ORGANIC SULFUR COMPOUNDS^a

MODEL COMPOUND	RECOVERED STARTING MATERIAL	YIELDS	
		PRODUCTS	
	0%	 (95%)	
	5%	 (90%)	
	96%	No reaction	
	87%	No reaction	
	98%	No reaction	
$(n-C_8H_{17})_2S$	90%	No reaction	
	36%	 (23%),  (34%), CH_3SO_3Na (55%)	
	29%	 (31%),  (18%),  (51%)	

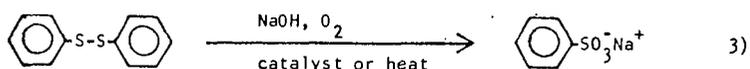
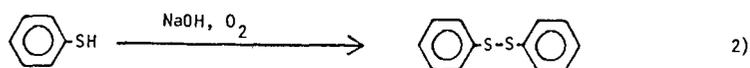
^a150°C, 200 psi O₂, 0.2M aqueous Na₂CO₃, 1 hour.

TABLE 2. EVALUATION OF POSSIBLE COAL CATALYSIS IN AMES PROCESS

Model Compound	Yield of Recovered Starting Material		
	Model Compound Alone	Lovilia Coal Added	
		N ₂	O ₂
Dibenzothiophene	96%	83%	76%
Diphenyl Sulfide	98	76	74
Diocetyl Sulfide	90	--	82
Benzyl Methyl Sulfide	36	75	13

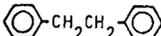
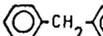
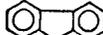
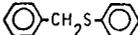
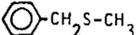
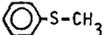
In order to take into account the decreased recovery expected due to adsorption of the model compounds onto coal, runs using both oxygen and nitrogen were performed. The results confirm that simple sulfides and dibenzothiophene, the principle functional groups expected to be in coal, are inert to oxidation under the Ames Process conditions.

Of the reactive functions, thiophenols are widely known to undergo facile air oxidation to disulfides (7) and the oxidation of thiophenols and disulfides to sulfonic acids under more forcing conditions is also known (8). That leaves the results of the reaction of two compounds, benzyl methyl sulfide and benzyl phenyl



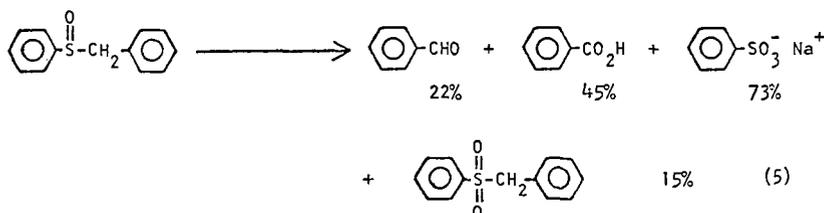
sulfide, to be explained. The fact that it is only the benzylic sulfides which are reactive is reminiscent of hydrocarbon autoxidation, a long known and well studied process which involves the free radical abstraction of hydrogen from weak carbon-hydrogen bonds (9). Table 3 presents the relative rates of hydrogen abstraction from some representative compounds by phenyl radical (10), the most studied of the hydrogen abstractors and t-butylperoxy radical (11), more closely similar to the peroxy radicals which we postulate would be the hydrogen abstracting species in the Ames Process, as well as the autoxidation rate of the pure compounds.

TABLE 3. RELATIVE RATES OF HYDROGEN ABSTRACTION BY FREE RADICALS

Compound	Ph \cdot , 60°C ^a	(CH ₃) ₃ COO \cdot , 30°C ^b	RH + ROO \cdot , 30°C ^b
	(1.0)	(1.0)	(1.0)
	3.6	5.0	2.3
	5.1	8.9	8.3
	13.	---	---
	17.	4.4	40.
	8.2	---	---
	1.4	---	---

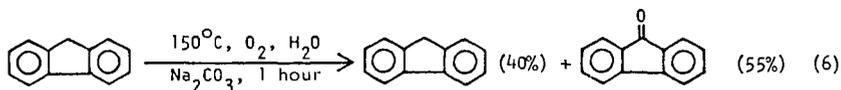
^aData of reference 10. ^bData of reference 11.

In order to rule out the possibility that the benzylic sulfides are in fact oxidized to either the sulfoxide or sulfone, which then are responsible for the observed products, both benzyl phenyl sulfoxide and benzyl phenyl sulfone were subjected to the reaction conditions. Because the sulfone is inert, it can be ruled out as a possible reaction intermediate. Although it does react, the sulfoxide gives sulfone as one of the products. Since sulfone is not isolated in the oxidation of sulfide under process conditions, the sulfoxide is also eliminated as a



possible reaction intermediate.

Beside benzylic sulfides, one would expect that some hydrocarbons, for example, fluorene, would also be reactive to the oxydesulfurization conditions. Under Ames process conditions, fluorene is indeed degraded to its known autoxidation product, fluorenone(13). While we have not yet run other hydrocarbons which might be expected to be reactive, we believe that they will behave similarly.



Fledgling studies of sulfur-containing synthetic polymers(14) add support to the model compound studies. Table 4 shows the results of subjecting three modified polystyrenes to the Ames Process conditions. Both the phenylthiomethyl and tolylthiomethyl polystyrenes are analogs of the model compound, benzyl phenyl sulfide. As we had anticipated, the solid polymers, which should be better models for solid coal, were reactive, but less so than the corresponding model compound. Polystyrene cross-linked by dibenzothiophene is unreactive, confirming the inertness of the dibenzothiophene moiety to oxydesulfurization.

TABLE 4. EFFECT OF THE AMES PROCESS ON SULFUR-CONTAINING POLYSTYRENE POLYMERS^a

Polymer ^b	%Sulfur Removed
$\text{P}-\text{CH}_2-\text{S}-\text{C}_6\text{H}_5$	10%
$\text{P}-\text{CH}_2-\text{S}-\text{C}_6\text{H}_4-\text{CH}_3$	20%
$\text{P}-\text{CH}_2-\text{DBT}-\text{CH}_2-\text{P}$	0

^a150°C, 200 psi O₂, 0.2 M aqueous Na₂CO₃, 1 hour.

^b P = polystyrene backbone; substituents are attached through the para position.

DBT = dibenzothiophene nucleus,

Finally, we have subjected the pyridine extract of an Illinois #6 coal to the Ames Process conditions. All of the sulfur in an extract is organically bound and hence, the quite accurate total sulfur determination is also the organic sulfur determination. The results in Table 5 show that oxydesulfurization apparently does not reduce the organic sulfur level of the extract. On the other hand, some of the extract is apparently oxidized as judged by the increase in S/C ratio, the increase in oxygen content, and the increased O/C ratio.

Our conclusions concerning the oxydesulfurization process as gleaned from model compound studies are, in summary, the following:

1. Thiophenols and disulfides are the only groups oxidized at sulfur.
2. Sulfides, including thiophenes, are not oxidized at sulfur.
3. Reactive sulfides are oxidized at reactive carbon-hydrogen bonds.
4. Reactive carbon-hydrogen bonds in functions not containing sulfur also react.
5. The Ames Process is directly analogous to hydrocarbon autoxidation.
6. More efficient sulfur removal without severe degradation of the coal is not possible under the present process conditions.

The success which these model compound studies have had in defining the limits of the efficacy of the Ames oxydesulfurization process encourage us to believe that this approach will be quite valuable in the evaluation of other proposed chemical coal cleaning techniques.

Table 5. EFFECT OF AMES PROCESS ON PYRIDINE EXTRACT OF ILLINOIS #6 COAL^a

Datum	Extract	Ames Processed Extract	
		N ₂ ^b	O ₂ ^c
Weight recovered	--	93%	85%
Elemental Analysis ^d			
C	76.6	77.9	68.5
H	6.1	5.8	4.9
S	0.8	0.8	0.9
O (by diff.)	14.4	12.8	22.3
S/C ratio (moles)	0.028	0.026	0.034
H/C ratio (moles)	0.95	0.90	0.85
O/C ratio (moles)	0.25	0.22	0.43

^a150°C, 0.2 M aqueous Na₂CO₃, 1 hour. ^b200 psi N₂ pressure. ^c200 psi O₂ pressure.

^dSamples contain a small amount of ash or NaCl. Element percents are expressed ash or NaCl free.

HPLC AND PHASE TRANSFER CATALYSIS
IN THE ANALYSIS OF OXIDATION PRODUCTS
OF LIGNITE LIQUIDS AND MODEL COMPOUNDS

Edwin S. Olson and Bruce W. Farnum

Grand Forks Energy Technology Center
Department of Energy
Box 8213 University Station
Grand Forks, North Dakota 58202

The objective of these studies was to develop new methods for the analysis of the types and quantities of aryl groups and alkyl groups present in the alkylarenes and hydroarenes which are major constituents of the liquefaction products derived from lignite coals. A number of oxidation reactions of light oil hydrocarbon mixtures and model compounds were investigated. In order to get high yield oxidation reactions, phase transfer catalysts were utilized in some of the reactions. Derivatization of the reaction products to give highly UV absorbing compounds facilitated the analysis of the products with HPLC.

Trifluoroperacetic acid has been described as a useful reagent for the analysis of alkyl groups since it easily degrades the aromatic rings present in the structure and gives aliphatic carboxylic acids incorporating the alkyl groups(1). Unfortunately, mixtures of products have been obtained from the oxidation of single compounds;(1,2) e.g., indan gave 27% succinic and 27% glutaric acids(1). Surprisingly, tetralin was reported to yield cyclohexene-1, 2-dicarboxylic anhydride as the only product (1).

Tetralin was oxidized at 60° using Deno's procedure(1) and the resulting acid mixture was converted to the p-bromophenacyl esters by refluxing with

p-bromophenacyl bromide in 50% ethanol-water at pH=6.8. The esters were analyzed on a 10 μ Spherisorb-ODS HPLC column using a programmed gradient elution of methanol-water (Figure 1C). The program was devised so that the monoesters can be eluted followed by the diesters (see Table 1). The major components of the product mixture were succinic, glutaric and adipic monoesters and diesters (Figure 1A). The peaks corresponding to the p-bromophenacyl monoester of cyclohexene-1,2-dicarboxylic acid and the ethyl p-bromophenacyl mixed ester were very small. Since a unique product was not obtained from tetralin nor from most other hydroaromatics and alkylarenes, it is difficult to see how any quantitative information about coal or coal oil structure can be obtained with this method of oxidation.

TABLE 1

Peak No.	Retention Time, (min.)	Compound
1	4.0	succinic mono ester
2	5.5	glutaric mono ester
3	7.4	adipic mono ester
4	15.9	p-bromophenacyl alcohol
5	20.3	p-bromophenacyl trifluoroacetate
6	21.5	p-bromophenacyl bromide
7	28.5	succinic diester
8	29.8	glutaric diester
9	30.1	adipic diester
10	17.2	mono p-bromophenacyl cyclohexene-1,2-dicarboxylate
11	28.8	p-bromophenacyl ethyl cyclo- hexene-1,2-dicarboxylate
12	34.5	di p-bromophenacyl cyclo- hexene-1,2-dicarboxylate

Oxidation of a light oil from the liquefaction of Beulah, N.D. lignite with synthesis gas at 460° and 27.5 MPa (3) was carried out with CF₃CO₃H-H₂SO₄. HPLC analysis (Figure 2) of the p-bromophenacyl esters of the reaction products exhibited peaks corresponding to a range carboxylic acids in the range of 4 to 9 carbon atoms.

The oxidation of aromatic rings with RuO₄ was investigated as an alternative to the trifluoroperacetic acid method. Since yields reported in the literature (4) vary

considerably for this reagent, the use of a phase transfer catalyst to bring the oxidizing agent for RuO_2 into the organic phase was studied. The reaction of tetralin in CCl_4 with NaOCl or NaIO_4 in water using RuO_2 and Adogen-464 (tetraalkylammonium salt) gave α -tetralone in low yield, rather than the expected product, adipic acid. The two phase oxidation of 1-methylnaphthalene with NaIO_4 in the presence of RuO_2 and Adogen-464 gave a good yield of phthalic acid and 3-methylphthalic acid. These were characterized by HPLC analysis of the p-bromophenacyl esters. The more easily oxidized naphthalene rings show greater promise in this type of analysis than the benzene systems.

A number of oxidizing agents are available for oxidation of aromatic hydrocarbons to the aryl ketones and aldehydes. A high yield reaction was desired for use in the quantitative analysis of lignite-derived oils which contain many methyl and other alkylarenes as well as hydroaromatics. HPLC analyses of the oxidation products and their 2,4-dinitrophenylhydrazones were carried out. The oxidation of tetralin to α -tetralone using ceric ammonium nitrate in nitric acid (5) could not be repeated. Instead the nitrate ester of tetralol was obtained. A similar product was reported for o-xylene oxidation (6). Using acetic acid as the solvent (7) produced the acetate ester of α -tetralol. A matrix of conditions was studied utilizing a phase transfer catalyst in the tetralin oxidation to determine maximum yield conditions. Thus a 74% yield of α -tetralone was obtained using a benzene-water system with Adogen-464, with no side reaction products.

Ceric ammonium nitrate oxidation of naphthalenes in two phase systems with Adogen-464 gave naphthoquinones and mixtures of products, thus this oxidizing system will be of limited usefulness in the study of naphthalenic and larger aromatic ring systems.

Adogen-464 was also very effective in catalyzing the oxidation of tetralin in benzene with KMnO_4 as the oxidant (8). Thus the "purple benzene" reagent gave a high yield, 90%, of α -tetralone.

Other oxidizing reagents, such as nitrobenzene and peroxydisulfate, which sometimes give aldehydes or ketones, were not successful in the model compound or light oil oxidation studies.

Experimental Section

Trifluoroacetic acid oxidations were performed as in Reference 1 and excess reagent destroyed with Pt/asbestos. Most of the trifluoroacetic acid was evaporated at low temp/pressure on a rotary evaporator. The pH was adjusted to 6.8 and an equal volume of ethanol was added. The solution was filtered and refluxed with p-bromophenacyl bromide for 15 minutes. The esters were extracted with ethyl acetate and analyzed with an Altex Model 332* liquid chromatograph with u.v. detection.

Ruthenium tetraoxide oxidations were performed by dissolving 0.3 g of organic substrate in 25 ml CCl_4 and adding to 2.0 g NaIO_4 in 25 ml water. Adogen-464 (Aldrich) (50 mg) and 20 mg RuO_2 were added and stirring continued overnight. A second 2.0 g of NaIO_4 were added and stirred overnight. Acids were extracted from the acidified aqueous layer and analyzed by HPLC after conversion to the p-bromophenacyl esters.

Ceric ammonium nitrate oxidations were performed by adding 10.5 g of the reagent in 40 ml water to 0.3 g organic substrate in 10 ml benzene or other solvent. Adogen-464 was added and the mixture stirred and heated at 60-65° for 3 hrs. A second 10.5 g of reagent in 15 ml water was added and heating continued for 5 hrs. Extraction of the mixture with pentane gave the carbonyl products. Permanganate oxidation was carried out similarly.

* Reference to specific brand names and models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

REFERENCES

1. N.C. Deno, B.A. Greigger, and S.G. Stroud, *Fuel*, 57, 455 (1978).
2. R. Liotta and W.S. Hoff, *J. Org. Chem.*, 45, 2887 (1980).
3. W.G. Willson, C.L. Knudson, G.G. Baker, T.C. Owens, and D.E. Severson, *Ind. Eng. Chem., Prod. Res. Develop.*, 18, 297 (1979).
4. U.A. Spitzer and D.G. Lee, *J. Org. Chem.*, 39, 2468 (1974).
5. L. Syper, *Tet. Letters*, 4493 (1966).
6. L.A. Dust and E.W. Gill, *J. Chem. Soc. C*, 1630 (1970).
7. W.S. Trahanovsky and L.B. Young, *J. Org. Chem.*, 31, 2033 (1966).
8. D.G. Lee and V.S. Chang, *Synthesis*, 462 (1978).

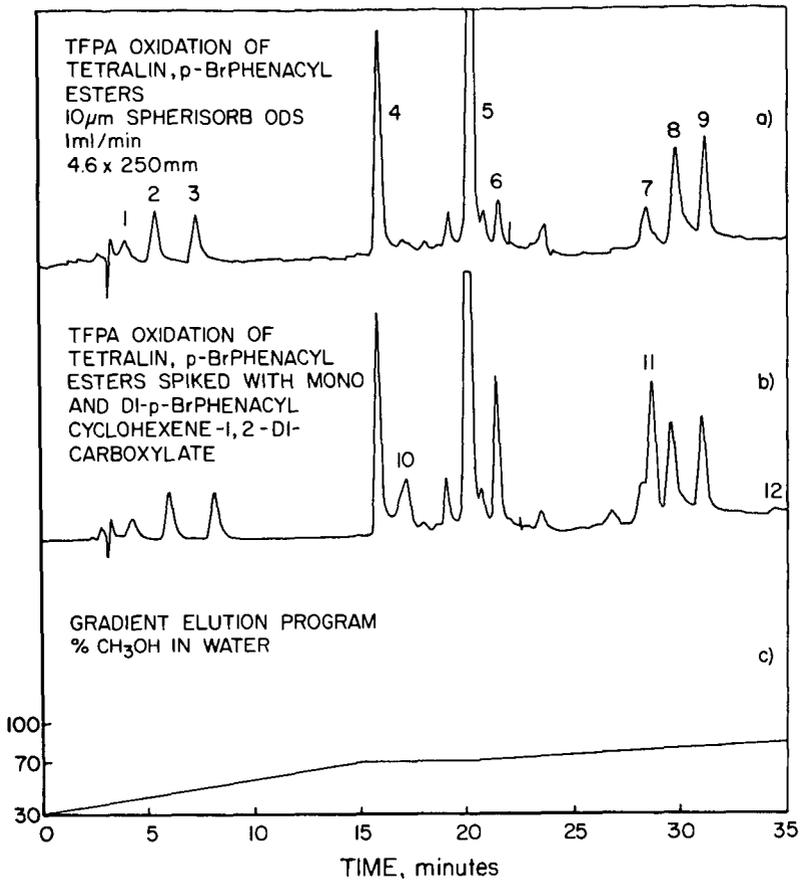


Figure 1. - Separations of p-bromophenacyl esters of tetralin TFPA oxidation products. Peak numbers refer to compounds in Table 1.

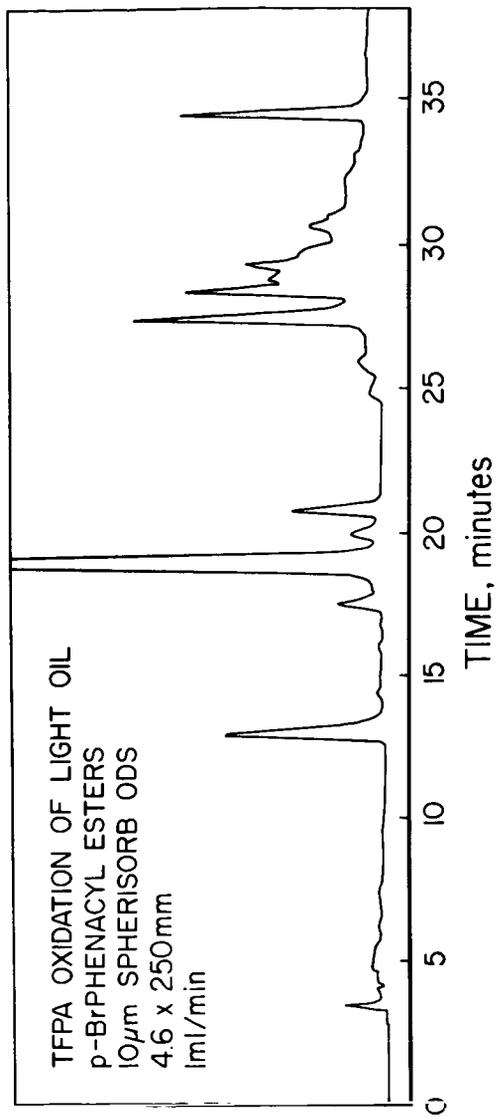


Figure 2. - Separation of p-bromophenacyl esters of light oil TFPAs oxidation products.

THE UTILISATION OF HYDROGEN IN UK COAL LIQUEFACTION

Glyn O. Davies and Derek F. Williams

NCB, Coal Research Establishment, Cheltenham, UK

INTRODUCTION

Though at present the North Sea wells provide all the crude oil that the UK requires, this is unlikely to be the case much beyond the end of the decade. As Britain has adequate large coal reserves, the National Coal Board is preparing for this situation by developing two processes to convert coal into liquid hydrocarbons. The main feature of these processes is that they are aimed at the production of premium products such as gasoline, diesel and jet fuels, a feature which could also prove attractive outside the UK.

When producing light hydrocarbons in high yield it is essential to utilise hydrogen efficiently as the production of hydrogen is expensive. In both processes this is achieved by a two-stage conversion. In the first stage the coal is extracted, in the absence of gaseous hydrogen, such that the mineral matter can be removed and the initial coal breakdown products can be stabilised. This makes it possible to use a selective catalyst in the second stage to hydrocrack and refine the coal extract.

The paper describes the two processes under development, and illustrates the utilisation of hydrogen with a set of material balance and hydrogen consumption data for the preparation of gasoline and diesel fuel.

THE PROCESSES

The two processes under development are the Liquid Solvent Extraction (LSE) process and the Supercritical Gas Extraction (SGE) process.

The LSE process involves the use of the high boiling (+ 300°C) fraction from the hydrocracker product to extract coal at about 400°C. Because no gaseous hydrogen is needed at this stage, the extraction is carried out at only a few atmospheres pressure, which is a considerable advantage where solids handling is involved. Sufficient hydrogen transfer to stabilise the extracted material is effected by virtue of the hydrogen donor property of the hydrogenated recycle solvent. High extract yields are obtained as virtually all of the coal except some of the inertinite/fusinite fraction is dissolved. Furthermore by a suitable choice of extraction conditions it is possible to produce a solution that has favourable filtration properties, ie low filtrate viscosity and high filter cake permeability(1).

The clean coal solution (0.04% ash) is reacted with hydrogen over a catalyst at about 425°C and 200 bar, as a result of which the aromatic structures present are hydrogenated and cracked, and oxygen, nitrogen and sulphur are removed. Some of the commercially available petroleum hydrotreating catalysts of the Co/Mo/alumina, Ni/Mo/alumina type are suitable for this duty but other specially formulated catalysts are being investigated.

The hydrocrackate is distilled into three fractions: a naphtha, nominally IPB-200°C, a mid-distillate (200-300°C) and a higher boiling fraction for recycle as coal solvent.

The naphtha is a stable colourless liquid which is rich in naphthenes and contains 13% hydrogen, 400 ppm nitrogen and 10 ppm sulphur. After further vapour phase hydrofining to reduce the nitrogen and sulphur to acceptable levels it can be dehydrogenated by reforming to produce a high octane gasoline. For example, in one test(2) the reformate produced in 95% yield had a RON of 108.

The mid-distillate is nearly colourless and is a mixture of two and three ring hydro-aromatics and naphthenes, and some aromatics. It contains 11% hydrogen, and, like the naphtha, only small quantities of heteroatoms. Batches of mid-distillates have been further hydrotreated to produce diesel fuel for engine tests. Saturation of the aromatic content raised the hydrogen composition to 13% and the overall performance of the fuel in the Ricardo(3) test engine was equivalent to that of current UK road vehicle fuel. It had a Cetane No of 46, and a Bosch Smoke Index that was half that of petroleum gas oil at high load. It had a very low freezing (-78°C) and low cold filter plugging point (-50°C) which indicated a complete absence of hydrocarbon waxes.

The naphtha, mid-distillate and hydrogenated mid-distillates have also been assessed as steam cracker feedstocks for the production of olefins and aromatics(2). Tests made by ICI gave good cracking patterns: 33% olefins and 24% aromatics, and ICI gave the hydrogenated mid-distillate a commercial value index of 95 compared with 100 for a standard petroleum naphtha.

In an integrated process as shown in Fig 1, coal is the only input and extra coal will be required to supplement the extraction residues to provide the hydrogen and process energy. Preliminary estimates from a study of a commercial scale plant have indicated an overall thermal efficiency of 65-70%.

The process has been developed at the Coal Research Establishment on a 2 kg/h scale. An integrated plant (Fig 2) has been run for long continuous periods, up to 1200 h, providing distillates for assessment and data for the design of larger plants. The design of a 1 tph plant has already been prepared and it is hoped to build it within the next two years. It should then be possible to go straight to a single stream plant consuming 2-5000 tpd and so to full scale commercial production by the mid-1990s.

The Supercritical Gas Extraction process (Fig 3) involves the use of an aromatic solvent close to its critical temperature to dissolve coal at about 420°C. In this condition the fluid is less dense and less viscous than a liquid would be, but the molecules are sufficiently close together to act as a solvent. At ambient conditions the solvent is a liquid so can be used to slurry the coal. The supercritical solvent selectively extracts the smaller molecular species which contain more hydrogen than the rest of the coal(4). The carbonaceous residue recovered after extraction is suitable for gasification and combustion to provide the process requirements as shown in the Figure. For high volatile bituminous coals, an extract yield sufficient to provide this overall balance, between 40% and 50% of the daf coal, can be obtained. This is also the case for lower rank coals, depending on their composition.

No hydrogen gas is needed in the extraction stage, but the nature of the solvent leads to an extraction pressure of 200 bar. Depressurisation of the supercritical solution stream causes the extract to be precipitated and allows the solvent to be recycled. The extract is hydrocracked, together with recycled heavy oil, to produce similar products to those obtained in the LSE process at an estimated overall thermal efficiency of 65%.

The SGE method of extraction has been demonstrated on a 5 kg h^{-1} scale, and will be studied at a scale of 1 tph as part of the test facility, already referred to in the LSE process description.

HYDROGEN UTILISATION

In order to illustrate the utilisation of hydrogen in NCB coal liquefaction one set of data for the LSE process has been considered in detail. The data were obtained from the integrated unit shown in Fig 2, when equilibrium conditions were assumed to prevail.

A UK bituminous coal - Annesley - was used and its composition is shown in Table 1. The yields of products and hydrogen consumption are given in Table 2. The liquid products, under the specified set of conditions, consisted of naphtha and mid-distillate and a considerable yield of pitch. The filter cake liquids shown were not recovered in the test but an estimate has been made in Table 2 of the effect of recovering these liquids by washing and passing them to the hydrocracker with the bulk of the extract solution.

The utilisation of hydrogen in the test is shown by the hydrogen account of Table 3. This shows that 66% of the hydrogen in the feedstock appears in the liquid products and is a quantitative measure of the efficiency of hydrogen utilisation during liquefaction.

As the naphtha and mid-distillate products are considerably refined during hydrocracking, their conversion to gasoline and diesel fuel requires little further hydrogen consumption. The final yield values are given in Table 4. The low gas yield in the overall process contributes significantly to the efficient utilisation of hydrogen and the relatively high thermal efficiency of the process.

The pitch obtained in the run studied can be reduced and possibly eliminated by employing more severe hydrocracking conditions. However, the pitch is a useful product as it could be used as an electrode binder, a source of carbon black or alternatively it could be coked to produce electrode carbon. Some coking tests have been made and the following yields obtained: coke 51%; distillates 39%; gas 10%. The liquid recovered in the latter case would supplement the solvent inventory of the process and would allow some of the lighter solvent to be removed as products.

Alternative options of this kind have been examined in a study of the commercial scale operation of the process carried out in conjunction with an International Chemical Engineering Contractor. The results from these studies showed that neither the plant cost nor the overall thermal efficiency varied greatly between the options.

The above data relate to the processing of bituminous coal. Lignites and brown coals can also be extracted by this process with the additional advantage that much of the high oxygen content in these coals is eliminated in the extraction stage as CO_x thus in principle saving hydrogen. It appears that when hydrogen gas is used during the extraction stage oxygen is removed as water. However although tests with brown coals and lignites have been made in laboratory experiments, no equilibrium processing data are as yet available.

CONCLUSIONS

The two liquefaction processes being developed by the National Coal Board offer the prospect of an efficient production of transport fuels from coal.

Test results from small pilot plant indicate yields, based on daf coal to liquefaction, of 14% gasoline and 35% diesel fuel, both meeting the current UK road fuel specifications. The hydrogen consumption in this test work was 6.7% daf coal and the hydrogen recovered in the liquid products was equivalent to 66% of the hydrogen fed to the process.

These yields do not represent the maximum values as an additional 21% high boiling liquid product was available for further conversion and alternative processing schemes for the conversion of this material are under investigation.

ACKNOWLEDGEMENTS

The authors wish to thank the National Coal Board for permission to present this paper. The views expressed are those of the authors and not necessarily those of the Board.

REFERENCES

1. Clark, J. and Rantell, T., Filtration Symposium, Inst. Chem. Eng., Event 231, Dublin 1980.
2. Davies, G.O., "Making Olefins and Aromatics from Coal Liquids", Coal Chem. 2000, Sheffield 1980.
3. Davies, G.O. and Freese, R.G., "The Preparation and Performance of Coal Derived Diesel Fuel", 14th C.I.M.A.C Conference, Helsinki 1981.
4. Whitehead, J. and Williams, D.F., "Solvent Extraction of Coal in Supercritical Gases", J. Inst. Fuel, Dec. 1975.
5. Kimber, G.M., Coal Research Establishment, Private Communications.

Table 1

Analysis of Annesley Coal

International Classification 633

Carbon	84.8% daf coal
Hydrogen	5.5% " "
Oxygen	7.5% " "
Nitrogen	1.9% " "
Sulphur	0.8% as received
Volatile matter	38.6% daf coal
Vitrinite	77%
Exinite	4%
Inertinite)	
Fusinite)	19%
Swelling number	6½

Table 2

Product Yields and Hydrogen Consumption in LSE Process Unit

<u>Material</u>	<u>Weight without cake washing</u>	<u>Weight with cake washing</u>
<u>Input</u>		
Coal (daf basis)*	100	100
Hydrogen consumed	5.7	6.0
<u>Products</u>		
C ₁ -C ₃ gases	10	10
C ₄ -170°C naphtha	13	13
170-350°C mid-distillate	29	35
> 420°C pitch	15	21
Cake liquids	17	4
Undissolved coal	12	12
CO _x , H ₂ O, H ₂ S, NH ₃	10	11

*This does not include the additional coal (approximately 60 parts by weight) needed to supplement the filter cake for process heat, power and hydrogen production.

Table 3

The Hydrogen Account for LSE Test Run

Conversion of 100 units daf coal

<u>Hydrogen In</u>		<u>Hydrogen Out</u>	
Coal (daf basis)	= 5.5	Filter cake	= 0.8
		Hydrocarbon gases	= 2.2
Hydrogen consumed	= 6.0	Heterogases	= 1.1
		Naphtha	= 1.8
		Mid-distillate	= 4.0
		Pitch	= 1.6
<hr/>			
TOTAL	= 11.5	TOTAL	= 11.5
<hr/>			
Hydrogen Retrieval	=	$\frac{\text{Hydrogen in Liquid Products}}{\text{Hydrogen in Coal + Added Hydrogen}} \times 100$	= 66%

Table 4

Products and Hydrogen

Consumption after Secondary Refining

<u>Material</u>	<u>Weight without cake washing</u>	<u>Weight with cake washing</u>
<u>Input</u>		
Coal (daf basis)*	100	100
Hydrogen consumed	6.2	6.7
<u>Products</u>		
C ₁ -C ₃ gases	10	11
Gasoline	13	14
Diesel fuel	29	35
Pitch	15	21

*This does not include coal needed for process heat, power and hydrogen production.

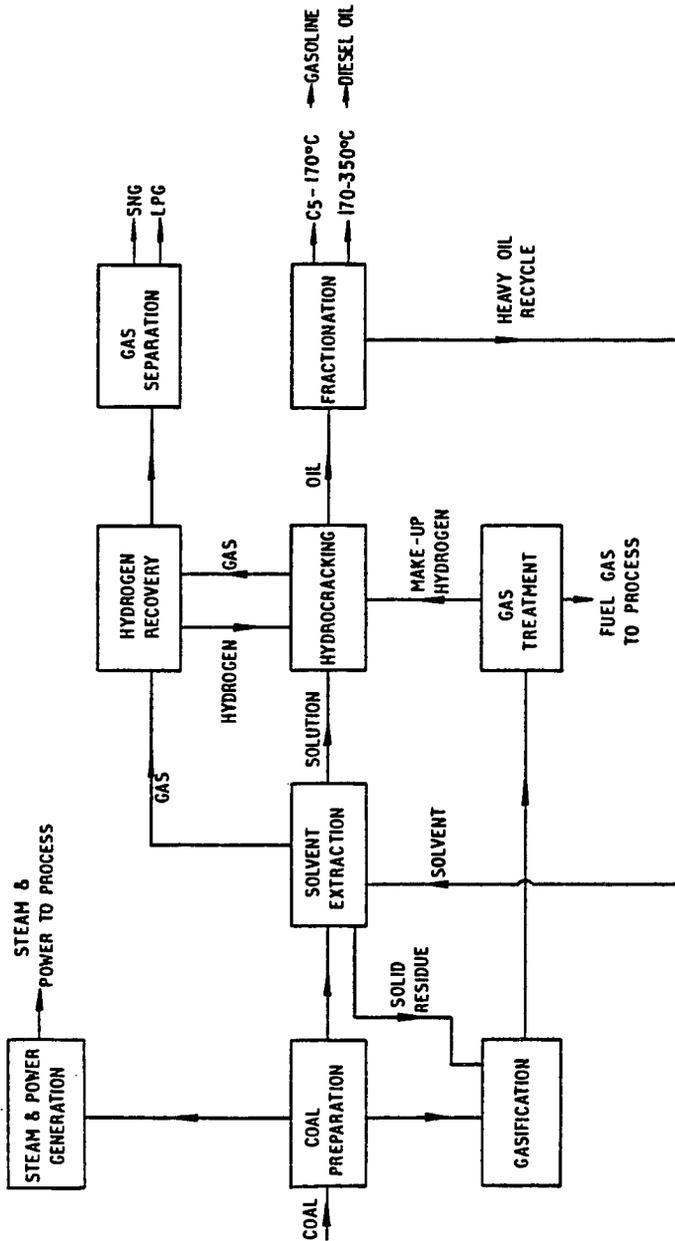


FIG. 1 NCB LIQUID SOLVENT EXTRACTION PROCESS

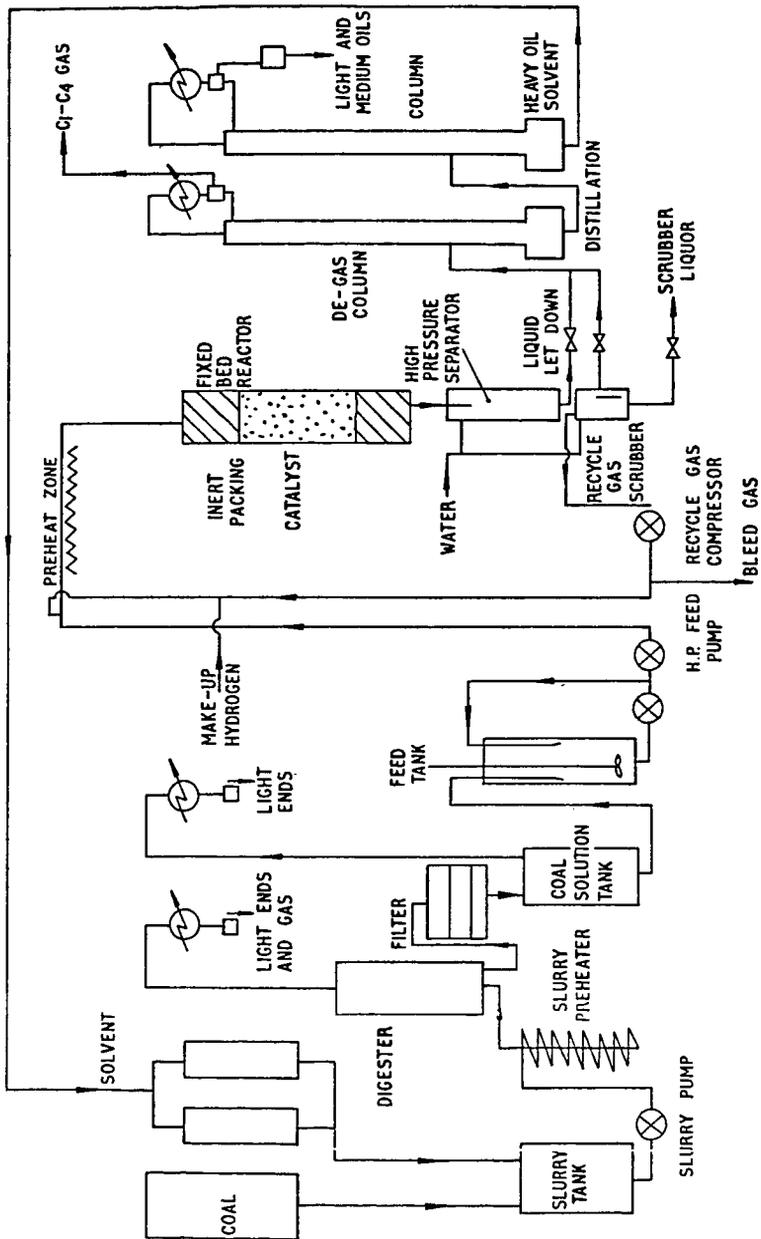


FIGURE 2. INTEGRATED SOLVENT EXTRACTION / CONTINUOUS HYDROCRACKING UNIT

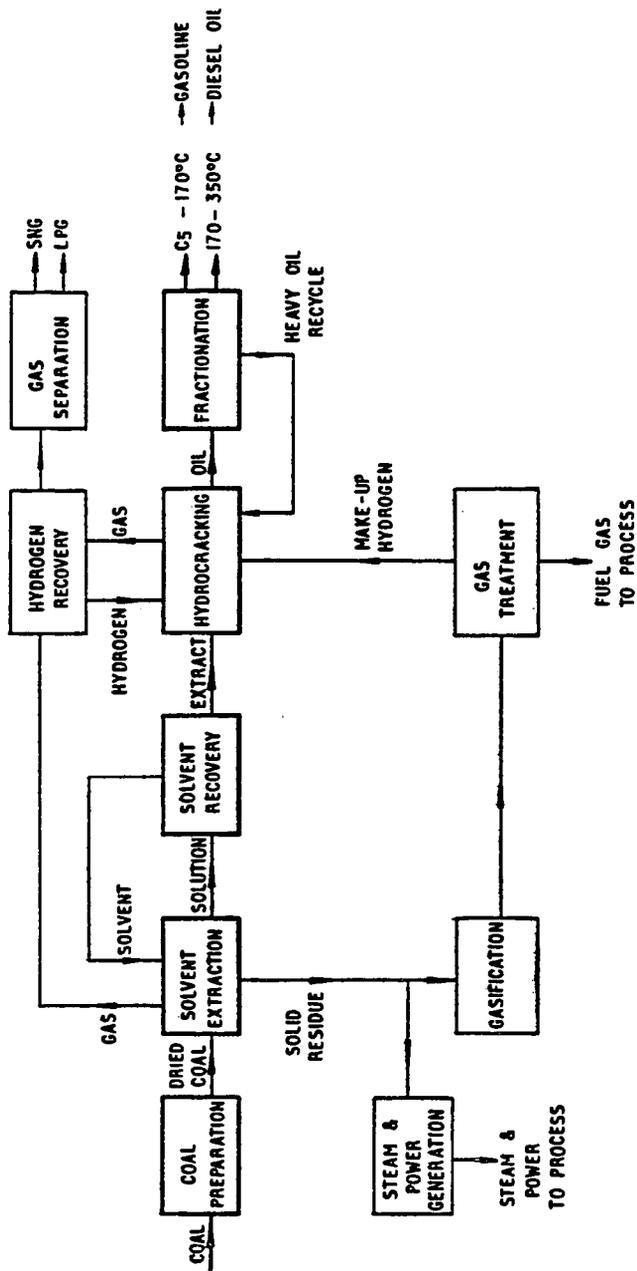


FIG. 3 NCB SUPERCRITICAL GAS EXTRACTION PROCESS

Hydrogenation of German bituminous coal for distillates
by I. Romey, F. Friedrich, B. Strobel

More than fifty years ago already, conversion of coal to oils, motor fuels, and chemical feedstocks was available in Germany on industrial scale. The first hydrogenation plant was commissioned in Leuna in 1927. This plant employed the sump-phase and gas-phase hydrogenation processes developed by Bergius and Pier. At the same time the Pott Broche process for production of coal extracts and the Fischer-Tropsch synthesis for production of motor spirit and chemical feedstock were under development in Germany. After World War II, no attempt was made to reactivate the coal liquefaction technology, primarily because of economical reasons. Only since the oil crisis in 1973 further development was done on sump-phase hydrogenation for production of distillate oils from coal. The present activities are shown on table 1.

Compared to the earlier German hydrogenation process the new developments are featured particularly by the following conditions:

- Removal of solids and residual oils from the hydrogenation process by distillation rather than by mechanical separation.
- Recycling of only distillate oil for coal slurry preparation which means reduction of asphaltene concentration in the hydrogenation reaction.
- Use of the distillation residue for production of hydrogen in a downstream gasification plant.

I. Romey, F. Friedrich, B. Strobel
Bergbau-Forschung GmbH
Franz-Fischer-Weg 61

4300 Essen 13

COMPANY	SITE (DISTRICT)	CAPACITY (COAL T/D)	BUDGET MM \$	SPONSOR	TIME SCHEDULE
					74 75 76 77 78 79 80 81 82 83 84
Bergbau- Forschung	Essen (Ruhr)	.5	16	State Gvt. NW (MWMV)	plant running
Ruhrkohle Veba Oel	Bohrup (Ruhr)	200	150		
Saarberg	Reden (Saar)	.5	4	Federal Gvt. (BMFT) and State Gvt. Saar	
	Völklingen (Saar)	6	28		
Rheinbraun	Wesseling (Rhein)	.25	3	Federal Gvt. (BMFT)	

Tab. 1: Current coal hydrogenation projects in Germany

By these modifications the following improvements can be achieved:

- Lowering of the process pressure down to 300 bar
- Increase of the specific reactor throughput
- Minimize the residue problems by only producing an easily disposable mineral slag.
- Substantially increase thermal efficiency and, thus, process economics.

The Experimental Plant

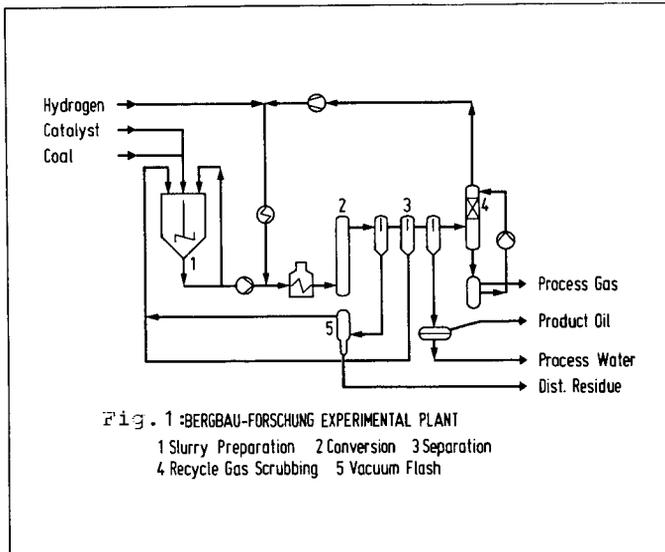
In an experimental plant of Bergbau-Forschung, Essen, work is done since 1976 on the modified hydrogenation process. Work meanwhile exceeds 100 test runs totalling more than 20 000 hours of operation under hydrogenation conditions. Typical run conditions for a German bituminous coal are shown on table 2.

EXPERIMENTAL PLANT OPERATION

Reactor temperature	°C	475
Preheater outlet temp.	°C	420
Make-up hydrogen	m ³ /kg maf coal	1.00
H ₂ -Partial pressure at preheater inlet	bar	250
Total pressure	bar	300
Coal throughput	kg/l hr	.5 to .75
Type of recycle oil	middle a. heavy distillate	
Solids concn. in slurry	%	> 40
Coal particle size	mm	< .1

Tab. 2: Typical run conditions for a German coal.

Fig. 1 shows a simplified flow scheme of the experimental plant.



A pumpable slurry is made up by ground coal, recycled distillate oil, and catalyst. The slurry is fed to the hydrogenation reactor via a pre-heater. Upstream the pre-heater high-pressure hydrogen is added. After leaving the reactor the hydrogenation products are led to a series of three high-pressure separators. From the first vessel high- and non-boiling oils are drawn off together with all the solids viz some unconverted coal, mineral matter, and catalyst. The liquid is treated in a vacuum flash unit to yield a distillate oil containing no solids. Mostly middle oil is obtained from the second separator and also used for slurry preparation. In the third separator the net product oil is recovered. It consists of only light oil and middle oil. The gases that also form under reaction conditions are for the most part hydrocarbons. They are removed from the recycle gas by high-pressure oil scrubbing.

All the oils and gases produced in the hydrogenation step need upgrading to give saleable products.

Typical oil yield C₅+ from German bituminous coal is around 50 % w/w, as was shown in BF experimental-plant runs under conditions listed in table 2.

Product Oil

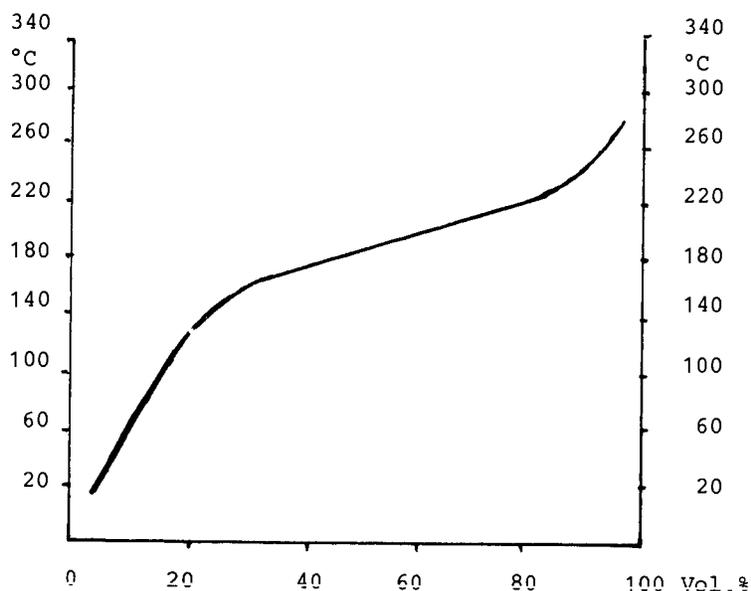
The distillate oil accounts for the largest portion of the product slate, i.e. for 50 % relative to the maf feed coal. The boiling point of the product oil, on average, ranges between 50 and 320°C, 30 % of the oil being in the boiling range below 200°C. Oil boiling above 320°C is not produced as net product with the new German coal hydrogenation process. It is all recycled and therefore out of the net balance.

So far no detailed breakdown of all the components contained in the coal oil can be given. Sure we do know roughly the oil composition in terms of group type analyses, and there is no doubt on what individual structures the mixture is basically composed of. However because of its origin the oil contains countless isomer compounds not only with regard to the carbon skeletons but also to the different partially hydrogenated aromatics. The product slate is further complicated due to the presence of phenol and its homologous compounds and to the presence of various nitrogen containing compounds. So only few individual compounds as phenol, all of the cresols, toluene, naphthalene, and tetrahydronaphthalene account for more than 1 % of the total oil quantity. A lot of compounds, however,

account for less than 0.1 per cent.
 Some data on the properties and analytical composition
 of the light and medium boiling oil fraction, respecti-
 vely, is listed below.

		Light Oil	Middle Oil
boiling range	°C	C ₅ - 200	200 ~ 325
density/15°C	g cm ⁻³	0.865	0.990
heating value	kJ kg ⁻¹	41 000	38 500
elemental analysis			
C	p.ct.,w/w	85.3	87.4
H	"	11.1	9.1
O	"	3.5	3.0
N	"	0.24	0.60
S	"	0.1	0.1
group type analysis			
neutral oil	p.ct.,w/w	84.35	77.3
phenols		15.4	16.2
bases		0.25	6.5

Figure 2 shows the boiling diagram of a typical product oil.



Residue

In the new German process all the remaining solids from the liquefaction step are kept in the flash distillation residue as is done also in some U.S. processes. In addition to the solids the residue contains the so-called asphaltoles, asphaltenes, as well as some heavy oil.

At elevated temperatures the organic matter forms a melt that keeps the solids suspended. Thus the residue represents a pumpable liquid that may easily be transferred to a pressurized gasifier. There by partial oxidation the hydrogen required for the liquefaction stage can be produced. Residue gasification is part of the overall process design but so far has not been investigated experimentally.

Approximately 25 p.ct. of the organic matter of the feed coal is bound in the flash distillation residue. The table gives information on the average analysis of such a residue.

Flash Distillation Residue Analysis

softening point	°C	180
volatile matter	p.ct., w/w	30
ash content	"	26
pyridine insolubles	"	52
asphaltoles	"	9
asphaltenes	"	21
heavy oil	"	18

Hydrocarbon Gases

In bituminous coal hydrogenation gas formation mainly consists of hydrocarbons. In the plant there are several different process gases having different composition. The question whether these streams either should be combined or treated separately can only be discussed in commercial scale design. In the experimental plant the different streams are only measured and analyzed. From the analytical results we compute the overall hydrocarbon gas production based on the feed coal. This information is listed in the following table:

Hydrocarbon Gases

		saturates	olefins
methane	p.ct. w/w maf. coal	6.8	
ethane	"	5.7	
ethene	"		0.1
propane	"	5.6	
propene	"		0.3
n-butane	"	2.8	
i-butane	"	0.7	
butenes	"		0.2
total		21.6	0.6
		22.2	

In coal liquefaction the hydrocarbon gases are regarded as unavailable by-products. Nonetheless, at least the C₂ through C₄ hydrocarbons can be commercialized as valuable chemical feedstocks or fuel gases.

Water and Inorganic Gases

The inorganic compounds water, hydrogen sulfide, and ammonia as well as carbon monoxide and carbon dioxide are basically formed as by-products of coal hydrogenation. The quantities produced depend on the heteroatoms content (oxygen, nitrogen, sulfur) of the feed coal. These heteroatoms are partly converted to form hydrogen compounds.

The oxygen contained in coal is partly removed during hydrogenation as carbon monoxide and dioxide, the monoxide presumably being formed from dioxide by reduction with hydrogen. The carbon dioxide originates via decarboxylation from carboxylic groups present in the coal.

The denitrification and desulfurization reactions taking place along with the degradation of the coal is to be considered an advantage. While upgrading coal oil the heteroatoms left have to be removed anyway. On the other hand, the formation of some water from oxygen in coal may be taken as a drawback because of the consumption of hydrogen and the removal of potentially valuable phenols.

The product water is let down from high pressure together with the net product oil, and the two layers formed are subsequently separated. Dissolved in the water there are some phenols and inorganic compounds. Carbon monoxide has only poor solubility in the liquids

so it has to be removed from the high pressure gas by continuous release of some recycle gas. Carbon dioxide, ammonia, and hydrogen sulfide however dissolve sufficiently in water to be easily scrubbed from the high pressure gas by injecting some additional water. Consequently inorganic salts such as ammonium carbonate and sulfides are also present. Refining the process waste water will accordingly need much effort in commercial scale liquefaction.

Hydrogen Consumption

Hydrogen consumption on maf feed coal is 6.5 to 7.5 per cent computed on the maf feed coal, as measured in the BF experiments under the conditions listed in table 2. The consumption values cover both the chemically reacted hydrogen and the unavoidable losses. These have been determined to be about 15 % on the total hydrogen consumption. In result, the hydrogen consumed in reaction amounts to 5.5 to 6.5 per cent on maf coal.

When reducing hydrogenation severity and thus the yields - only 40 % instead of 50 % for oil, and 13 % instead of 23 % for gas - correspondingly the chemical hydrogen consumption is reduced to 4 %.

Because of the many different ways the hydrogen reacts with coal and the intermediate products, it is difficult to determine what amount of hydrogen is actually consumed with each of it. Methane for instance maybe formed from primary, secondary, and tertiary carbon atoms initially bound in coal. Each way implies a different hydrogen requirement.

Status of Development

The data and experiences from the BF experiments have been used to support design and engineering work on a 200 t/d pilot plant. The process flow sheet is essentially identical to the one of the experimental unit. Presently this demonstration project is under construction near Bottrop/Essen, Germany. The plant will be operational in mid - 1981. The program is under the responsibility of Ruhrkohle AG and Veba Oel AG, and the State Government of Northrhain-Westfalia gives major financial support.

INTERACTIONS BETWEEN SOLVENT COMPONENTS, MOLECULAR HYDROGEN AND MINERAL MATTER DURING COAL LIQUEFACTION

by F. J. Derbyshire, P. Varghese and D. D. Whitehurst

Mobil Research and Development Corporation
P.O. Box 1025, Princeton, New Jersey 08540

INTRODUCTION

In direct coal liquefaction, the principal objective is to stabilize the molecular fragments generated by the thermal degradation of coal. Preferably, this is achieved by capping the coal-derived free radicals with hydrogen. In turn, this requires that hydrogen is provided at a rate and in a form compatible with the demand established by the thermal reaction of the coal.

Although the ultimate source of hydrogen is hydrogen gas, the most effective route for hydrogen transfer is by way of the liquefaction solvent. Hydrogen is supplied most readily from hydrogen donor compounds which generally are replenished by catalytic reactions (either externally or internally). In the absence of an adequate concentration of active donors, free radicals can be stabilized by other reactions between solvent components and coal (1).

Extensive studies have been carried out in this laboratory to examine the mechanisms of coal liquefaction in both donor and non-donor solvents. The ultimate aims of this research are to provide means of identifying and controlling the optimal recycle solvent composition in a given process.

In earlier reported work (2) certain polycondensed aromatics were identified as effective non-donor coal solvents. These compounds react with molecular hydrogen during coal liquefaction forming low concentrations of active donors, in situ. The process can be catalyzed by coal mineral matter components. In addition, it is considered that the ability of these components to effectively disperse the coal liquefaction products also contributes to their efficacy.

It is recognized that the study of single model compounds, while affording useful information, does not take into consideration the more complex situation in a real solvent where solvent-solvent interactions undoubtedly occur (1). As a first approach to this problem, the previous studies have been extended to investigate coal conversion in a binary solvent system consisting of a conventional donor (tetralin) and polycondensed aromatics. The results of these investigations are presented below.

EXPERIMENTAL PROCEDURE

Experiments were conducted with bituminous (Monterey) and sub-bituminous (Belle Ayr) coals. The coals were prepared from 1-2" diameter lumps which had been stored under an argon atmosphere (without drying) in a refrigerated room since sampled from the mine. The lumps were crushed and sieved to minus 100 mesh in a glove bag under flowing argon. When sufficient sample had been ground, it was thoroughly mixed and then sealed in small vials, still under argon. A different vial was used for each experiment, the required quantity of coal being weighed from a newly opened vial and the remainder discarded. Analyses of the prepared coals are shown in Table 1.

The conversions were carried out in a small stirred autoclave which has been described in detail elsewhere (1). Essentially this is a reactor of about 12 cc. capacity heated by a close fitting electric furnace. Agitation is provided through the movement of an oscillating plunger which is driven by an electromagnet. A relatively large free volume above the reactor is

kept cold which acts as a gas reservoir allowing operation under virtually isobaric conditions.

The reactor was loaded with a mixture of solvent and coal in the ratio of 3:1 on a dry coal basis. After pressurizing the reactor, the system was heated to the desired temperature with agitation. The time required to reach reaction temperature was an additional 30 minutes. Reproducibility of temperature profiles was good as were the calculated conversions. Several sets of repeated experiments showed a variation of less than $\pm 3\%$ in conversion.

At the end of the reaction, a quantity of tetrahydrofuran (THF) was injected into the reactor while still under pressure following which it was quenched using an ice/water bath. The objective of injecting THF was to facilitate the removal of the solid reaction products (e.g. when pyrene was the solvent) from the reactor.

After venting, the reactor contents were removed in more THF and transferred to a Soxhlet extraction thimble where they were continuously extracted in THF for 18-24 hrs under argon. Conversions were calculated on the basis of the insoluble residue.

The soluble products were analyzed by gas chromatography and GC/MS.

RESULTS AND DISCUSSION

Experiments were carried out to investigate the dissolution of Belle Ayr and Monterey coals in mixtures of pyrene with tetralin and 2-methylnaphthalene with tetralin. The effects of donor concentration, gas atmosphere and hydrogen pressure on coal conversion and hydrogen transfer from tetralin were determined. In addition, some experiments were conducted to examine the reactions between pyrene, tetralin and hydrogen gas.

Coal Conversions

Conversion to THF soluble products and gases is shown as a function of tetralin concentration for Belle Ayr and Monterey coals in Figures 1 and 2 respectively. The reactions were carried out at 400°C for 1 hr under 1000 psig gas pressure. On the two figures, data are presented showing conversions in pyrene-tetralin mixtures both in argon and in hydrogen and, for comparison, in 2-methylnaphthalene-tetralin mixtures in the presence of hydrogen.

For both coals, the conversion in the absence of a donor was enhanced by the presence of gaseous hydrogen. As has been shown (2), the conversion obtained in pyrene is higher than in a less condensed compound such as 2-methylnaphthalene and its effectiveness as a solvent is related to the formation of dihydropyrene during liquefaction.

With reference to Figure 1, the effect of adding tetralin up to about 8 wt% appeared to have little effect on conversion in the three systems shown. Further increase in the donor concentration was accompanied by increasing conversion which reached a limiting value of about 85% at tetralin concentrations of about 70% and above. At the high donor levels, the conversion was not

apparently affected by the nature of the other component or by the gas atmosphere. The major differences between the solvent systems are evident at tetralin concentrations between 8-70%.

From the Figure it is apparent that hydrogen gas is beneficial. However, at a given tetralin level methylnaphthalene based solvents with hydrogen show only a modest improvement over pyrene based solvents without hydrogen. In marked contrast pyrene based solvents respond dramatically to hydrogen pressure and at only 30% tetralin, the blended solvent is almost as effective as 100% tetralin.

The same general effects are observed for the conversion of Monterey coal, Figure 2. In this instance, the two lower curves are not parallel. However, the conversion in 2-methylnaphthalene shows approximately proportional dependence on tetralin concentration whereas in the pyrene-tetralin-H₂ system there is again a major increase in conversion with as little as 15% tetralin.

It has previously been reported that the presence of molecular hydrogen can increase coal conversion in solvents which have low donor capacity (3). The data presented here confirm these findings and also demonstrate that the effect of hydrogen gas is dependent upon the chemical structure of the other compounds present. In particular, the combination of a polycondensed aromatic (pyrene) with a donor in the presence of hydrogen behaves synergistically with respect to coal conversion.

Effect of Hydrogen Pressure

The influence of hydrogen pressure on the conversion of the two coals is shown as a function of donor concentration in Figure 3. The pressures examined were 1000 and 1800 psig.

There was no apparent effect due to hydrogen pressure, over this range, for the conversion of Belle Ayr coal. However, with Monterey coal, the effect of increasing pressure was to increase the conversions in pure pyrene and to some extent, in pyrene-tetralin mixtures to that obtained in pure tetralin. From the standpoint of maximizing conversion of Monterey coal, at high hydrogen pressure, there is little benefit to be derived from the addition of tetralin. This is not to state that the quality of the liquefied products is independent of donor concentration.

The effects of hydrogen pressure during coal conversion have been reported for the Exxon EDS process when operating in a mode where vacuum tower bottoms were recycled (4). Such a recycle stream would be expected to contain a proportion of polycondensed aromatics and compounds with similar chemistry. It was found that increasing the hydrogen pressure from 1500 to 2500 psig gave improved conversion and improved selectivity to lighter products for a range of coals including ones similar to those reported here.

The different responses of the two coals studied here may be partly attributable to differences in their respective mineral matter compositions. It has been

reported that the hydrogenation of pyrene is related to the coal pyritic iron content (2) which is much higher for the Monterey coal.

Hydrogen Transfer

It is commonly known that the extent of coal conversion is related to the hydrogen consumed in the process. Under given reaction conditions, the quantity of hydrogen required is independent of solvent composition. At any given time, the majority of hydrogen is supplied by the most labile source.

It may be assumed that, in the systems described, tetralin is the preferred hydrogen source. For each experiment, the amount of hydrogen made available by tetralin dehydrogenation was calculated, correction being made for isomerization to methylindan. It was found that in the pyrene-tetralin-H₂ system, less hydrogen was made available by tetralin dehydrogenation than in pure tetralin for a comparable conversion level. At lower tetralin concentrations in the mixed solvents, it does not appear that the amount of tetralin was a limiting factor since its dehydrogenation to naphthalene was always less than 40%. Supporting this contention earlier studies (1) have shown that a variation of tetralin concentration from 4 to 43 wt% in Monterey coal conversion, resulted in similar conversions but with corresponding tetralin dehydrogenations of 86 to 8% respectively.

The relative effect of the other solvent component and the gas atmosphere on hydrogen transfer from tetralin is shown in Figure 4 for both coals at a selected level of conversion. In these examples, the tetralin concentration differs since, as shown on Figure 1 and 2, the required concentration to attain a particular conversion is dependent upon the other system components. It can be seen that the required donor capacity for coal conversion is dependent upon the nature of the coal and of the other components present. The implication is that there is considerable potential for economy in donor consumption by judicious control of the solvent composition.

From the previous work with pyrene alone (2) it seems probable that the reduced hydrogen transfer from tetralin is due to part of the hydrogen demand being met by the transfer of molecular hydrogen to the coal through the formation of dihydropyrene. Such a mechanism is not as readily available with 2-methylnaphthalene as it is more difficult to reduce with hydrogen. There was no evidence of the presence of 2-methyltetralin in the reaction products where 2-methylnaphthalene was used as a solvent component.

Thermal Reaction of Pyrene and Tetralin

Some experiments were conducted to investigate the reactions between pyrene, tetralin and hydrogen gas in an attempt to elucidate reasons for the observed synergism. The results are summarized in Table 2 and show the extent of pyrene hydrogenation under the different conditions studied.

It can be seen that pyrene was thermally hydrogenated by reaction with hydrogen gas and under these conditions, its conversion to dihydropyrene was low (0.6%). The extent of hydrogenation was increased by the addition of iron pyrites. These findings are consistent with previous results relating conversion in pyrene to coal mineral matter catalysis (2).

In an inert atmosphere, in the presence of tetralin, 5.7% of the pyrene was hydrogenated. This result is particularly significant as it establishes that tetralin can transfer hydrogen to pyrene producing a substantial concentration of a more active donor. The same experiment conducted under molecular hydrogen resulted in a still greater degree of pyrene hydrogenation which was higher than would be predicted from a purely additive effect.

The foregoing results suggest that there may be several different mechanisms to effect H-transfer in systems which contain donors and polyaromatic compounds. Some possible alternatives are discussed below.

Neglecting direct interaction of hydrogen gas with coal derived free radicals, there appear to be four possible routes for H-transfer:

- 1) Tetralin + R → Naphthalene + R-H
- 2) Tetralin + Pyrene → Naphthalene + Dihdropyrene
- 3) Pyrene + H₂ → Dihdropyrene
- 4) Dihdropyrene + R' → Pyrene + R-H

Reaction 1) is the conventionally regarded process of hydrogen transfer from a donor. Reaction 2), it has been shown, can take place thermally and is promoted by molecular hydrogen. Reaction 3) can occur thermally and is catalyzed by coal mineral matter. Reaction 4) is parallel to reaction 1) and presumably proceeds at a faster rate.

In pure tetralin, reaction 1) prevails and in pure pyrene, reactions 3) and 4) take place. In pyrene-tetralin mixtures under hydrogen, all four reactions are possible and on this basis an explanation for the observed synergism in conversion and for the reduction in hydrogen transferred from tetralin is proposed.

The combined effect of reactions 2) and 3) is to generate a higher concentration of dihydrodropyrene than when 3) alone is possible. Dihydrodropyrene would be preferred to tetralin as the hydrogen donor since it has been shown that depletion of donors is essentially sequential (1). That is, until the most active donor is reduced to a low level, there is little significant contribution from the next most labile hydrogen source.

The ensuing increase in dihydrodropyrene concentration due to H-transfer from a low concentration of tetralin, especially in the early stages of reaction, could account for the observed synergism. In addition, some of the net hydrogen demand will be met via reaction 3) which will reduce the amount of hydrogen which otherwise would be predominantly supplied by the tetralin. It is anticipated that economies in donor concentration and consumption observed in these model compound studies would be observed in a process such as EDS when operating with bottoms recycle.

This explanation is tentative and there are many other factors which have not been considered, among which are the differences in solubility and dispersive properties of pyrene and tetralin and their mixtures. The outcome of these studies shows that there are potential advantages to coal liquefaction through an improved understanding of solvent chemistry which can lead to the selection and control of solvent composition. Some benefits of selected solvent recycle have already been observed in practice (4, 5, 6) and improvements such as those found in these model compound mixtures could significantly affect the viability of a coal liquefaction process.

SUMMARY

Studies of coal conversion in mixtures of pyrene, 2-methylnaphthalene and tetralin have shown that:

- 1) Mixtures of pyrene and tetralin in the presence of hydrogen gas have been found to be synergistic in coal conversion. At tetralin concentrations as low as 15 wt%, the conversion was almost as high as that in pure tetralin.
- 2) There is no similar synergistic effect when 2-methylnaphthalene is substituted for pyrene. The ease of reduction of pyrene is considered to be one reason for this different behavior.
- 3) With pyrene-tetralin mixtures in hydrogen, the hydrogen supplied by the donor at a given level of coal conversion is considerably reduced.
- 4) Reactions between pyrene, tetralin and hydrogen gas in the absence of coal showed that pyrene can be hydrogenated by reaction with molecular hydrogen alone and by tetralin alone. In combination with tetralin and hydrogen, the extent of pyrene hydrogenation is further enhanced.

ACKNOWLEDGEMENT

This work was conducted under Electric Power Research Institute (EPRI) Contract No. RP-1655 which is jointly funded by EPRI and Mobil Research and Development Corporation. Mrs. L. F. Atherton is the EPRI Project Manager.

REFERENCES

1. D. D. Whitchurst, M. Farcasiu, T. O. Mitchell and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," Third Report Under EPRI Project RP-410, December 1979.
2. F. J. Derbyshire and D. D. Whitchurst, paper presented at the EPRI Contractors' Meeting, May, 1980, Palo Alto, California.
3. L. E. Furlong et al., paper presented at the 1975 National AIChE meeting, Los Angeles, California.
4. L. L. Ansell, K. L. Trachte and J. W. Taunton, paper presented at the EPRI Contractors' Meeting, May 1980, Palo Alto, California.
5. J. A. Kleinpeter and F. P. Burke, Proceedings of the EPRI Contractors' Meeting, May 1979, Palo Alto, California.
6. H. E. Lebowitz and C. J. Kulik, Proceedings of the EPRI Contractors' Meeting, May 1979, Palo Alto, California.

Table 1
Properties of Coals

	<u>Belle Ayr</u>	<u>Monterey</u>
Elemental Analysis (m.f.)		
% C	72.20	75.18
H	5.65	5.82
O	20.56	12.78
N	1.19	1.38
S	0.40	4.34
Ash	4.50	11.19
Sulphur Forms		
Pyritic	0.03	0.68
Sulphate	0.03	0.75
Organic	0.35	2.97
Total	0.41	4.40

Table 2
Thermal Reactions of Pyrene, Tetralin and Hydrogen

Solvent	Gas	Time (mins)	Temp (°C)	Pressure (psig)	% Pyrene Conversion to Dihydropyrene
Pyrene	H ₂	60	400	1000	0.6
92% Pyrene/8% Iron Pyrites	H ₂	60	400	1000	2.5
50% Pyrene/Tetralin	Ar	60	400	1000	5.7
50% Pyrene/Tetralin	H ₂	60	400	1000	8.6

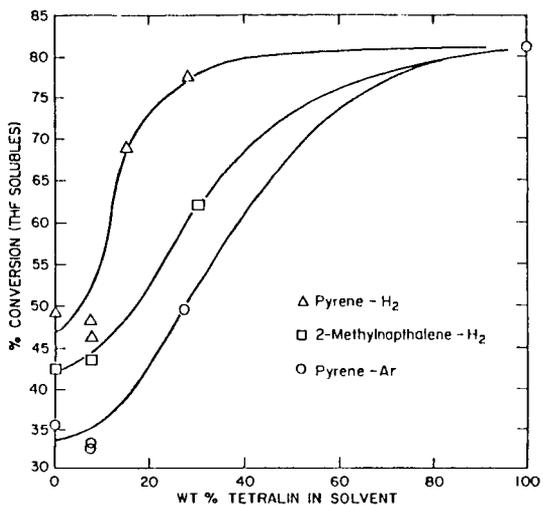


Figure 1. Conversion of Belle Ayr Coal in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr, 1000 psig)

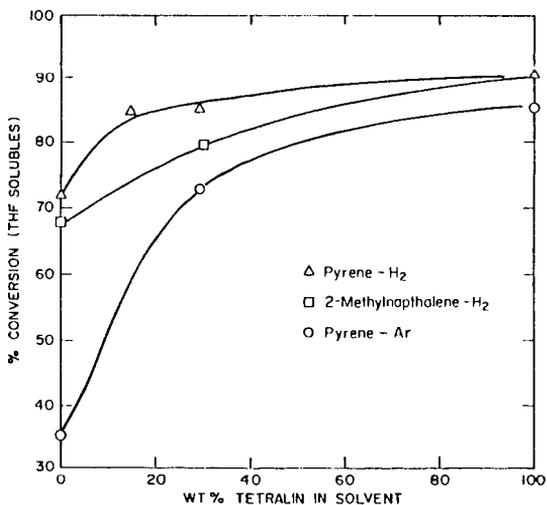


Figure 2. Conversion of Monterey Coal in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr, 1000 psig)

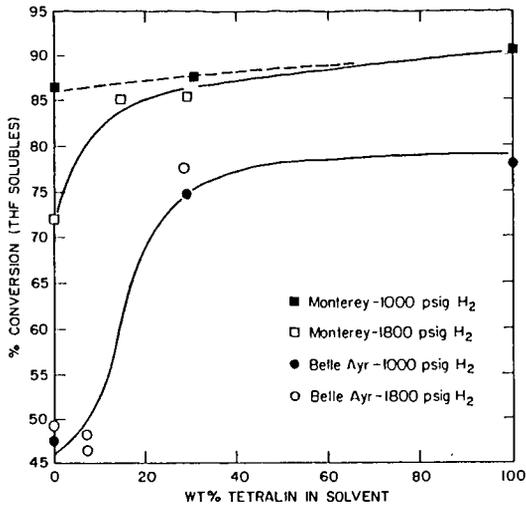


Figure 3. Effect of H₂ Pressure on Coal Conversion in Donor-Non-Donor Solvent Mixtures (400°C, 1 hr)

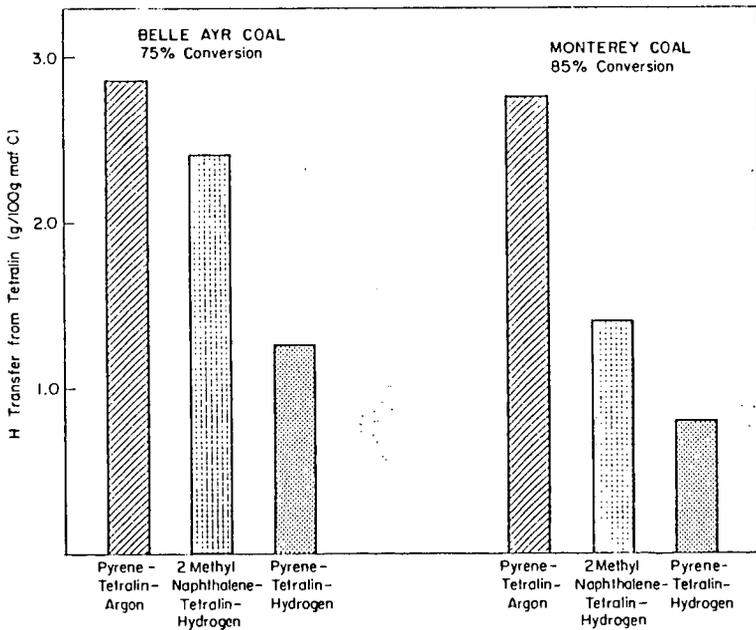


Figure 4. Effect of Solvent and Gas Atmosphere on Hydrogen Transfer (400°C, 1 hr, 1000 psig)

Evaluation of the Donor Ability of Coal Liquefaction Solvents

Bradley C. Bockrath and Richard P. Noceti

United States Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, Pennsylvania 15236

INTRODUCTION

Hydrogen donor solvents are used in most processes for the direct liquefaction of coal. The overall performance of these solvents depends on several qualities, including the abilities to physically solvate coal and its liquefaction products, to hold coal particles in suspension, to assist transfer of hydrogen from the gas phase to coal by dissolving molecular hydrogen or undergoing hydrogenation/dehydrogenation cycles (hydrogen shuttling), and to donate hydrogen directly to coal. Unknown factors may also be involved. In addition, in the case of commercial application, the solvents must be derived from coal and be suitable for recycle operation as well. In order to fully understand the function and importance of liquefaction solvents, the influence of each property must be studied separately. As a step towards this goal, we have developed a method by which the relative hydrogen donor ability of liquefaction solvents may be evaluated.

Our method of evaluation is based on a generally accepted hypothesis of the mechanism of coal liquefaction that has been used to rationalize the kinetics of coal liquefaction (1,2) and has been discussed several times in recent reports (for example (3,4,5)). According to this mechanism, the initial act is rupture of the weaker covalent bonds in coal. This produces two free radicals in close proximity. These radicals may either abstract hydrogen from any available source (donor solvent, coal or molecular hydrogen), undergo rearrangement, or add to some other site on either coal or solvent. Recombination or addition may lead to production of insoluble or char-like residues that are clearly undesirable. One critical function of the donor solvent is to provide a source of hydrogen. Abstraction of hydrogen by coal-derived free radicals prevents retrogressive reactions that lead to higher molecular weight products, and it directs more coal along the desired pathways to lower molecular weight products. Thus, donors with high potential for hydrogen transfer are regarded as beneficial to increased liquefaction yields.

Our approach to evaluation of the donor property was to devise a test that embodies the main features of the free radical mechanism of coal liquefaction. The basic idea is shown in Figure 1. Benzyl radicals are generated by the thermolysis of a convenient precursor at relatively low temperatures. These radicals then behave like the free radicals generated by the thermolysis of coal at liquefaction temperatures. When benzyl radicals are generated in a donor solvent, the relative amounts of toluene and bibenzyl produced reflect the relative ability of the solvent to donate hydrogen and to prevent recombination. A variable amount of benzyl radical is also lost, which presumably represents that amount which adds to or combines with the solvent.

As precursors to benzyl radical, we have used both dibenzylidiazene and dibenzylmercury. Both decompose at convenient rates at moderate temperatures (130-170°C) (6,7). The initially formed reaction products were found to be stable at these relatively low temperatures. Thus their yields, determined after decomposition of the precursor, represent the actual quantities of products formed as a result of the primary reactions.

Other methods have been used in the past to provide a "solvent quality index." Notably, measurement of liquefaction yields produced under specified conditions and with a specified coal has been used to provide a direct empirical evaluation of solvent quality (8,9).

Various spectroscopic methods have also been used to estimate the relative amount of benzylic or hydroaromatic hydrogen available for transfer (10,11,12). These methods serve their intended purposes well. In the present work, we aim at developing a better understanding of the chemistry of liquefaction and the overall performance of liquefaction solvents by isolating the hydrogen donor ability and free radical scavenger ability for study.

RESULTS AND DISCUSSION

Since many of the compounds to be tested as model hydrogen donors are solids at room temperature, it was worthwhile to use an inert liquid as a diluent. Tert-butylbenzene served this purpose well. It possesses only relatively inert aromatic and primary aliphatic hydrogen and sufficient solvent power to dissolve most of the donor solvents to be tested. Decomposition of either benzyl radical precursor in tert-butylbenzene solution produced only small yields of toluene.

Material balance studies showed that not all of the benzyl radical present in the precursor was recovered as either toluene or bibenzyl. A sizeable fraction is apparently removed by side reactions with the solvent. In pure t-butylbenzene, this accounted for 24% of the benzyl radical, while in a 50/50 wt mixture of t-butylbenzene and tetralin, it accounted for 32%. In the gas chromatograms of the decomposition products, new peaks appeared which were due to high boiling compounds. In the case of runs done in the presence of tetralin, GC/MS analyses indicated that three of these peaks had the correct molecular weights for benzyltetralins, benzyl-naphthalene and bitetralyl. These products must arise from radical combination and addition reactions.

The appearance of solvent combination and addition products is in accord with some recently reported results from other groups. Collins et. al. (13) reported that after they heated coal with ^{14}C labeled tetralin at 400°C for 1 hour, the pyridine solubles were 1.6 wt. percent tetralin and the residue 2.6 wt. percent tetralin. In another experiment (13), ^{14}C labeled 1,3 - diphenylpropane was heated with tetralin at 400°C for 1 hour. Toluene and ethylbenzene were major products. In addition, methyl-naphthalenes, methyl-dihydro-naphthalenes, phenylethyltetralins, and phenylethyl-naphthalenes were found. A mechanism was proposed that involved combination of phenylethyl with tetralyl radical, followed by further thermolysis to produce methyl substituted tetralins and naphthalenes. Thus at higher temperatures, radical addition to solvent may be followed by subsequent thermolysis of the newly formed bridge. Evidence for the addition and subsequent dissociation of benzyl radical with tetralin at temperatures of $400\text{--}450^\circ\text{C}$ has also been reported by workers at Gulf (14). Another piece of evidence showing the importance of addition reactions is the report (15) that negative solvent balances were found during preheater studies. These findings were interpreted to mean that during the initial phase of liquefaction ($300^\circ\text{--}400^\circ\text{C}$), coal-derived solvent became bound to the coal so tightly that it could not be freed by either distillation or solvent extraction. Subsequent reaction after reaching 450°C changed the solvent balance to positive. Processes analogous to the addition/dissociation reactions described by Collins may be involved.

Taking this evidence together, it is apparent that an additional mode of action of donor solvent is that of free radical scavenger by combination and addition reactions. Accordingly, three indices were devised to compare donor solvents; the donor, the scavenger, and the combined index.

$$\text{Donor Index} = \frac{\text{Toluene}}{2 \text{ Precursor}}$$

$$\text{Scavenger Index} = \frac{2 \text{ Precursor} - (\text{Toluene} + 2 \text{ Bibenzyl})}{2 \text{ Precursor}}$$

$$\text{Combined Index} = \frac{\text{Precursor} - \text{Bibenzyl}}{\text{Precursor}}$$

These indices are based on mole ratios.

Since the combined index is merely the sum of the other two, we really have two independent measures of two different solvent qualities. The donor index may be taken as the relative amount of benzyl radical which abstracts hydrogen, and the scavenger index as the relative amount of benzyl radical which adds in some manner to the solvent. The scavenger index is determined by difference, being that fraction of benzyl which does not appear as toluene or dibenzyl.

Initial experiments were carried out with dibenzylidiazene and a series of model donor compounds. Although we were able to obtain satisfactory data with dibenzylidiazene, we have come to prefer using dibenzylmercury because it is far more stable in storage. We have found that dibenzylidiazene decomposes spontaneously over the course of several days by various pathways. This instability made it necessary to prepare the diazene immediately before use and to assay its purity by determination of the amount of nitrogen evolved upon decomposition of a known weight of crude material. By contrast, dibenzylmercury may be stored without significant decomposition for months. Thus with dibenzylmercury, the amount of benzyl added to each reaction mixture could be carefully controlled and was usually held constant at 0.87 wt. percent, based on the hydrocarbon portion of the precursor.

The three solvent indices were determined for the decomposition of dibenzylmercury for several solvent mixtures made from different amounts of tetralin in *t*-butylbenzene. The data contained in Figure 2 show that the donor index increases with increasing tetralin concentration. Also shown in this figure are data taken from reference (16) for conversion of a bituminous coal to pyridine soluble material after reaction for three minutes at 427°F in mixtures of tetralin with methylnaphthalene, cresol, and picoline. Conversion as well as the donor index goes up as the tetralin concentration in the solvent increases. This comparison is made only to point out the qualitative similarity between the two results since we assume that both coal conversion and toluene yield are related to the relative hydrogen donor ability of the solvent. In both cases the greatest increase in conversion or toluene yield comes at relatively low tetralin concentration.

The series of model compounds in Table I were evaluated using dibenzylidiazene as the source of benzyl radical. In each case the donor was diluted to 50 wt. percent in *t*-butylbenzene. These data show that the donor ability as measured by this method is indeed variable. The relative order of donor ability of the hydrocarbons is mostly as expected. Both hydroaromatic compounds—tetralin and 9,10-dihydrophenanthrene—are distinctly better than either *t*-butylbenzene or 1-methylnaphthalene. Indan has the highest donor index of the hydrocarbons in Table I. This is noteworthy in view of the prejudice often voiced against indanyl structures. Rearrangement of hydroaromatic compounds in recycle solvents to indanyl structures is often said to be detrimental. However, indan seems to be a good rather than poor donor, although its capacity to shuttle hydrogen by dehydrogenation cycles is still open to question.

In the first case, the donors in Table I have been compared at equivalent weight percent concentrations. This relates more directly to their use in practice and is more convenient when making comparisons among actual coal-derived solvents. However, if the assumption is made that essentially all hydrogen donated comes from benzylic sites, the donor index may be expressed on the basis of the molal concentration of benzylic hydrogen. The molal donor indices shown in Table I should relate more directly to the reactivity of individual benzylic hydrogens than does the simple donor index. In this comparison, benzylic hydrogen on indan is ranked between those on dihydrophenanthrene and tetralin. An important factor contributing to indan's superior rank measured on a weight basis is that benzylic hydrogen accounts for a relatively larger fraction of its weight.

The heteroatomic substituted compounds in Table I are also found to be relatively good donors, with the exception of tetrahydroquinoline. A striking aspect of this data is that the heteroatomic compounds all have relatively high scavenger indices. Their combined indices are therefore distinctly higher than any of the hydrocarbon species. Said another way, the

yields of the product of recombination, bibenzyl, are found to be smaller in the presence of these heteroatomic compounds than in the hydrocarbons. Tetrahydroquinoline has been reported to be a superior solvent for coal liquefaction (17,18). Also, esr experiments have shown that the concentration of free radicals in mixtures of coal and solvent after treatment at liquefaction conditions was roughly a factor of six smaller in the case of tetrahydroquinoline (or tetralin) than naphthalene (19). Tetrahydroquinoline's superior quality has been attributed to a unique combination of readily donatable hydrogen with a heightened ability to solvate coal and its liquefaction products due to the presence of both aromatic and polar functionality. In view of its high scavenger index, an additional reason for the superior liquefaction performance of tetrahydroquinoline may be its ability to add to or combine with free radicals initially produced by the thermolytic reactions of coal.

Table 2 contains the donor indices obtained for several coal-derived liquefaction solvents selected to provide a range of quality from poor to satisfactory. In all of these cases, the scavenger index could not be obtained because the bibenzyl peak was buried within the broad envelope of unresolved peaks usually associated with gas chromatograms of coal-derived liquids. All of the donor indices in Table 2 were obtained using dibenzylmercury as the source of benzyl radical. Note that in this case the donor index for tetralin is somewhat different than that in Table 1. We attribute this to the change in precursor from diazene to mercurial. The precision of both determinations is about the same.

Anthracene oil, cresote oil, and Panasol are generally considered poor performers in coal liquefaction. They also have the lowest donor indices in Table 2. Panasol is not a coal-derived liquid, but it is largely made up of mono-, di-, and tri-methyl-naphthalenes, which are frequently also major components in coal-derived liquids. Its donor index is essentially the same as that found for methylnaphthalene. By comparison, the index determined for a distillate cut from a SRC-II recycle solvent is higher, although not as high as that for tetralin.

Comparison of the donor indices with other available quality criteria is made with two sets of solvents. The DCD series are recycle solvents derived from Blacksville coal under different processing conditions in the 1000 lb/day liquefaction unit at PETC. The values of IR were derived as recommended (10) from the ratio of absorbances at 3040 and 2930 cm^{-1} due to aromatic and aliphatic hydrogen, respectively. Higher ratios reflect a greater degree of hydrogenation or relative aliphatic hydrogen content. In this comparison, there is a qualitative agreement between the two methods. That is, the donor index increases with the degree of hydrogenation of the recycle solvent.

The second set of solvents—F2, F14, and F16—provide a comparison of liquefaction yield versus donor index. In this case, liquefaction yield refers to benzene soluble yield from Wyodak coal after heating to 440°C and immediately cooling in a two liter autoclave under hydrogen pressure (2000 psi, cold) at a 2/1 solvent-to-coal ratio (20). F2-HV is the 500°F + distillation residue from a lightly hydrogenated recycle oil made in the Wilsonville SRC pilot plant from Wyodak coal. F-14 is a lightly hydrogenated recycle oil made in the Tacoma SRC pilot plant from Kentucky coal. F-16 is a coal gasification tar from an in situ gasification project near Hanna, Wyoming. These three solvents were selected because the liquefaction yields clearly distinguish the order $F14 > F2 > F16$. The donor indices are in the same order. However, the reported IR values (20) are not in this order. The relatively high IR values and results from other methods of characterization (20) indicate that all of these solvents, F16 in particular, are highly hydrogenated. In this case, the optimum hydrogen content may be closer to that of F14. Hydrogenation of solvents beyond certain limits has been shown to be detrimental because aliphatic structures begin to replace hydroaromatic structures (16,20).

Taken together, these data indicate that there is good qualitative agreement between liquefaction performance and the donor index. The ability of solvents to donate hydrogen to a free benzyl radical is an indication of how well they may donate to a typical free radical site formed on coal during liquefaction. We are now developing refined methods designed to yield more quantitative comparisons among hydrogen donor solvents.

EXPERIMENTAL

MATERIALS: All compounds that were purchased were reagent grade or equivalent and were used as received except as noted. Tetrahydronaphthalene (Tetrafin, Fisher) was trickled through a dry-packed column of activated alumina immediately before use and stored under argon. This treatment removed and prevented reformation of tetralin hydroperoxide and tetralone, which had been found to be present in all tetralin samples received. Dibenzylmercury (ALFA) was recrystallized once from absolute ethanol (m.p. 109-110° uncorr) and vacuum dried before use.

METHODS: Bis (phenylmethyl) diazene was prepared according to established procedures by the oxidation of N,N'-dibenzylhydrazine with freshly prepared mercuric oxide. (21,22). The diazene decomposes in air at room temperature but could be stored over a period of weeks at -10°C under argon. It was necessary to assay it before each use. This was done by measuring the nitrogen evolution on thermolysis in *t*-butylbenzene at 170°C. A mercury filled gas buret and leveling bulb proved satisfactory and gave a precision of about 2% absolute. Benzyl radicals were generated by thermolysis of either dibenzylmercury (7) or bis (phenylmethyl) diazene in a reaction vessel at selected temperatures between 130 and 210°C. The radical precursor was present at concentrations of 1-2 wt.% in various mixtures of donor solvents and *t*-butylbenzene. Each vessel was assembled from a 1/2" 316SS swagelock union and two end plugs and had a capacity of about 2 mL. The vessels were sealed after loading and maintained at temperature in a convection oven for 12-16 hours to ensure complete decomposition of the radical precursors. Product analyses were carried out on a HP5830 gas chromatograph with a six foot carbowax 20M (10% on chromosorb W) column, using internal standards. Each sample was analyzed in duplicate. Several unknown peaks were identified on a DuPont 21-490 MS after separation by an attached Varian 3700 G.C.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of their colleagues at PETC, especially Charles Schmidt for obtaining the GC/MS analysis, Donald Krastnan and John Ruether for providing samples from the operation of the 1 tpd liquefaction unit, and Sidney Friedman for helpful discussions. We are also indebted to Prof. Howard Silver of the University of Wyoming for providing samples of donor solvents.

TABLE I. SOLVENT INDICES OF MODEL HYDROGEN DONOR SOLVENTS*

COMPOUNDS	DONOR	SCAVENGER	COMBINED	DONOR/ α -CH**
	0.09	0.24	0.33	
	0.27	0.32	0.59	0.0178
	0.31	0.23	0.53	0.0279
	0.35	0.30	0.65	0.0207
	0.13	0.45	0.58	0.0123
	0.18	0.62	0.81	
	0.32	0.46	0.78	
	0.28	0.56	0.84	
	0.40	0.41	0.81	

*Determined by decomposition of dibenzylidiazene in solvent mixtures composed of 50/50 wt/wt of t-butylbenzene and donor. Estimated precision is ± 0.02 , based on triplicate determinations for tetralin.

**Donor index divided by molal concentration of benzylic hydrogen.

TABLE 2. DONOR INDICES OF COAL-DERIVED LIQUEFACTION SOLVENTS

<u>SOLVENT</u>	<u>DONOR INDEX*</u>	<u>$\bar{I}R$</u>	<u>LIQUEFACTION YIELD**</u>
Tetralin	0.41		
Anthracene Oil	0.21		
Creosote Oil	0.17		
Panasol	0.14		
SRC-II Distillate	0.31		
DCD 12/1	0.24	2.2	
DCD 12/26	0.28	2.7	
DCD 13/5	0.24	2.0	
F2-HV	0.32	9.2**	83.6
F14	0.45	6.1**	93.6
F16	0.29	12.7**	63.2

*Obtained using dibenzylmercury in 50 wt. per cent solutions with t-butylbenzene. Precision (2σ) estimated as ± 0.03 based on six replicates.

**Values taken from Reference 20.

REFERENCES

- 1) G. P. Curran, R. T. Struck and E. Gorin, *Ind. Eng. Chem., Process Des. Dev.*, 6, 166 (1967).
- 2) W. H. Wiser, *Fuel*, 47, 475 (1968).
- 3) D. D. Whitehurst, T. O. Mitchell, M. Farcasiu and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals," EPRI Final Report AF-1298 (1979).
- 4) R. C. Neavel, *Fuel*, 55, 237 (1976).
- 5) I. Wender and S. Friedman, *Proc. 13th. IECEC (San Diego, CA., Augut, 1978) Vol. 1*, p. 457.
- 6) B. K. Bandlish, A. W. Garner, M. L. Hodges and J. W. Timberlake, *J. Am. Chem. Soc.*, 97, 5856 (1975).
- 7) K. C. Bass, *J. Organometal. Chem.*, 4, 1 (1965).
- 8) Method No. 43080-60, Analytical Department, Catalytic, Inc. Wilsonville, Alabama.
- 9) J. A. Kleinpeter, F. P. Burke, P. J. Dudt and D. C. Jones, "Process Development for Improved SRC Options," EPRI Interim Report, AF-1158, August, 1979, Palo Alto, Calif.
- 10) C. H. Wright and D. E. Severson, *Preprints Am. Chem. Soc., Div. Fuel Chem.*, 16(2), 68 (1972).
- 11) K. S. Seshadri, R. G. Ruberto, D. M. Jewell and H. P. Malone, *Fuel*, 57, 549 (1978).
- 12) B. T. Fant, "EDS Coal Liquefaction Process Development: Phase IIIA," Annual Technical Report, 1 Jan - 31 Dec 1976, ERDA No. FE-2353-9 (1977).
- 13) C. J. Collins, B.M. Benjamin, V.F. Raaen, P. H. Maupin and W. H. Roark, *Preprints, Am. Chem. Soc., Fuel Div.*, 22(5), 98 (1977).
- 14) D. C. Cronauer, D. M. Jewell, Y. T. Shah, R. J. Modi and K. S. Seshadri, *Ind. Eng. Chem., Fundam.*, 18, 195 (1979).
- 15) M. G. Thomas and R. K. Traeger, *Preprints, Am. Chem. Soc., Fuel Div.*, 24(3), 224 (1979).
- 16) D. D. Whitehurst, T. O. Mitchell, M. Farcasiu and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals, Volume 1," EPRI Final Report AF-1298, pg. 1-46 (1979).
- 17) R. Bruecker and G. Koelling, *Brennstoff-Chemie*, 46, 23 (1965).
- 18) D. Hausigk, G. Koelling and F. Ziegler, *Brennstoff-Chemie*, 50, 8, (1969).
- 19) L. Petrakis and D. W. Grandy, *Fuel*, 59, 227 (1980).

- 20) H. F. Silver and R. J. Hurtubise, "Effect of Solvent Characteristics on Wyodak Coal Liquefaction," Final Technical Progress Report," Department of Energy Report FE-2367-9 (1979).
- 21) S. G. Cohen, S. J. Groszos and D. B. Sparrow, J. Am. Chem. Soc., 72, 3947 (1950).
- 22) J. R. Shelton and C. K. Liang, Synthesis, 204 (1971).

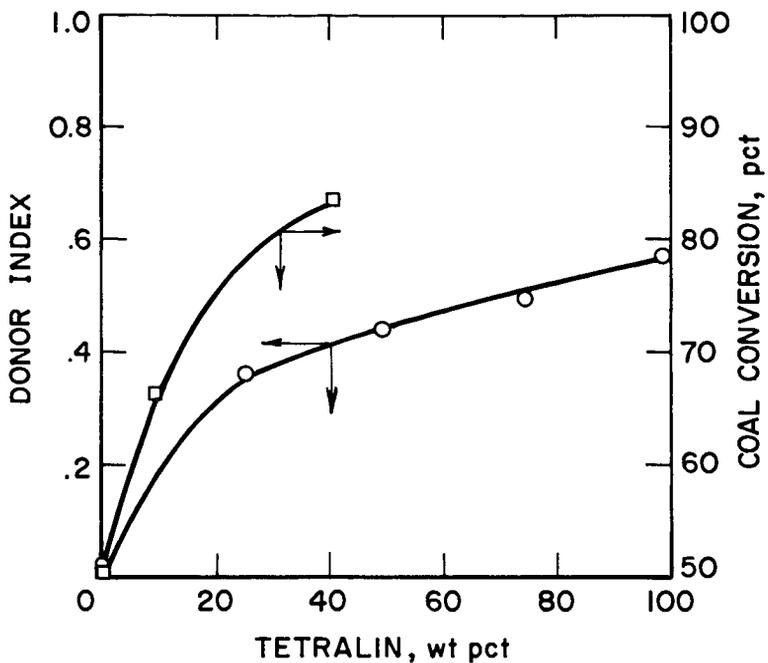


Figure 2.- Donor index of Tetralin/*t*-butylbenzene mixtures, ○, and coal conversion in synthetic solvents of different tetralin concentration, □, (from ref. 11).

9-24-80 L-17884

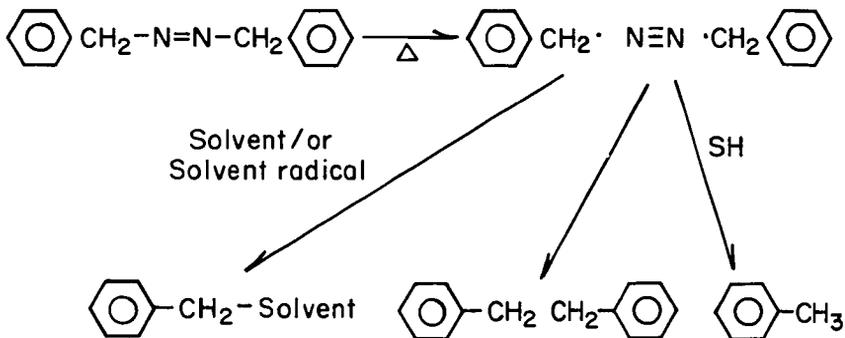
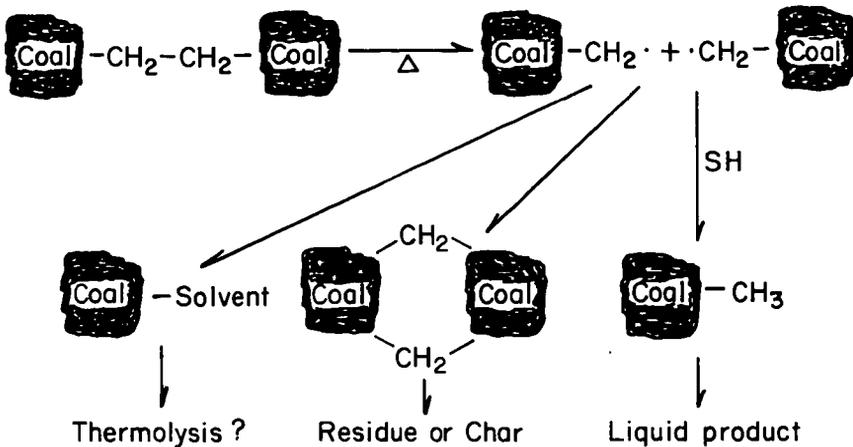


Figure 1.- Simplified hypothetical mechanism of coal liquefaction and its analog.

9-24-80 L-17885

RADICAL PATHWAYS OF COAL DISSOLUTION IN DONOR MEDIA DURING REACTIONS OF COALS AND SPECIFICALLY DEUTERATED TETRALIN*

James A. Franz and Donald M. Camaioni

Battelle, Pacific Northwest Laboratory
Battelle Boulevard, Richland, Washington 99352

INTRODUCTION

Recent studies utilizing deuterium labelling to trace the pathways of hydrogen transport between donor solvent, coal, and model compounds in the laboratories of Professor Leon Stock (Univ. of Chicago), Drs. L. A. Heredy, R. P. Skowronski and J. J. Ratto (Rockwell International) and in our own laboratory promise to provide a detailed understanding of mechanistic pathways operating at the molecular level during coal dissolution in donor media. Deuterium scrambling in donor solvents constitutes a sensitive probe of the structural features of coal and mineral matter. In previous papers^{1,2} we presented detailed information concerning the time dependence of the structural distribution of deuterium transferred to a subbituminous coal at 427°C in tetralin-1,1-d₂. In a preliminary report³ of our recent studies of high temperature reactions of specific radicals in the tetralin and alkylindan systems we presented evidence that 2-tetralyl as well as 1-tetralyl radical is formed during the oxidation of tetralin to naphthalene. The evidence for the intermediacy of 2-tetralyl was the observation of scrambling of deuterium from the 1- to the 2-position of tetralin during reaction with coal. In this paper we present a study of the scrambling and depletion of deuterium in reactions of a bituminous and a subbituminous coal with tetralin-1,1-d₂. Radical and ionic pathways responsible for major differences in scrambling rates for the two coals are discussed.

EXPERIMENTAL

Materials

Two coals were used in this study: Illinois #6 (Monterey) bituminous coal (C, 76.8%, H, 4.8%, S, 3.2%, N, 1.61% dry maf basis, 4.8% ash) and Kaiparowitz subbituminous coal (C, 77.3%, H, 1.2%; S, 0.8%; N, 1.2% dry maf basis, 8.5% ash). The coals were ground to -300 U.S. mesh and dried at 80°C and 10⁻² Torr.

*This work was supported by the U.S. Department of Energy, Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, under contract DE-AC06-76RLO-1830, with Battelle Memorial Institute.

Tetralin-1,1-d₂ was prepared as described previously² except that the byproduct dihydronaphthalene was removed by treatment of the mixture of tetralin-1,1-d₂ and dihydronaphthalene with sufficient Br₂ to consume dihydronaphthalene followed by distillation of the lower boiling tetralin.

Procedure for the Reactions of Coals and Tetralin-1,1-d₂

Coal (0.75g) and Tetralin (1.5g) were loaded in a 3 in x 3/8 in Swagelok-capped type 316 stainless steel tube. The tube was plunged in a molten lead bath maintained at a suitably higher temperature such that the bath would attain the desired temperature (427 ± 5°C) within approximately one minute. The tube was withdrawn after the desired reaction time, quenched in water, and worked up as follows: The contents of the tube were washed into a beaker with tetrahydrofuran (THF), ca. 75 ml. The THF solution and fines were centrifuged for several minutes. The THF solution was decanted and the fines washed and centrifuged two more times to remove soluble material. The THF solutions were combined and concentrated to ca. 2 ml and added to 250 ml of pentane above a 0.45 μm Millipore filter. The preasphaltenes and asphaltenes precipitated and were collected on the filter and washed with three portions of pentane. Small portions of the pentane solutions were saved for gc analysis to determine methylindane, tetralin, and naphthalene yields. The pentane solutions were concentrated to an oil in a small flask which was attached to a short path vacuum distillation apparatus and tetralin, naphthalene and methylindane et al. were removed at 150°C and 10⁻¹ Torr, leaving the light oils behind. The tetralin/naphthalene mixture was separated into its components by preparative gc or by preparative liquid chromatography.

Deuterium Analysis

Isolated tetralin and naphthalene were first examined by proton-decoupled ²H Fourier transform nuclear magnetic resonance (FTNMR) spectroscopy (12.211 MHz) using a Varian model FT-80 instrument. The tetralin samples were then spiked with toluene-d₈ and reexamined by ¹H FTNMR. The toluene methyl resonance lies conveniently resolved between the two aliphatic resonances of tetralin. The toluene-d₈/tetralin ratio as determined by gas chromatography (gc) was used in conjunction with the toluene-d₈/tetralin FTNMR integral ratios to calculate the total isotope level in the recovered tetralin. The recovered tetralin and naphthalene were also examined by gc/mass spectrometry to determine the distribution of labeled species.

RESULTS AND DISCUSSION

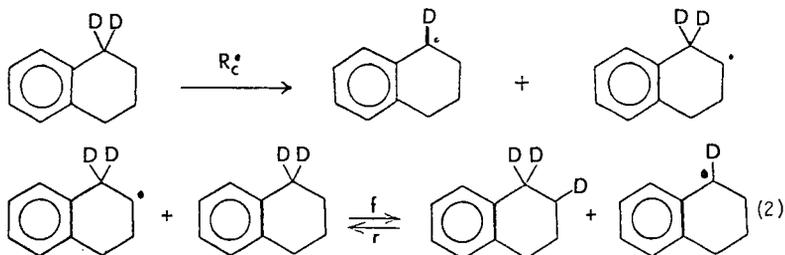
The distributions of deuterium label in the recovered tetralin and naphthalene are shown in Table 1. For Kaiparowitz coal, deuterium in the 1-position of tetralin decreases from 100% to 78% after 60 minutes' reaction. For Illinois No. 6, the deuterium content falls from 100% to 39% after 60 minutes, and the degree of scrambling is greater after only 5 minutes than the 60 minute reaction of Kaiparowitz. Incorporation of deuterium in the 2-position of tetralin to the extent of 11% occurs in 5 minutes with Illinois No. 6 but required 60 minutes with Kaiparowitz. A completely random distribution of deuterium would lead to 33% label in each of the aromatic 1- and

2-positions. The Kaiparowitz reaction was well short of complete scrambling at 60 minutes, but the Illinois No. 6 approaches complete scrambling at 35 minutes.

The exchange of deuterium between coal and tetralin occurs in both cases. Table 2 shows that about 25% of the label is lost from tetralin for either coal in 60 minutes. The rate of label loss appears slightly faster for Illinois No. 6 in the shorter reaction times. The total hydrogen uptake, by the two coals, as measured by the conversion of tetralin to naphthalene, is identical for the two coals at 10 minutes' or less reaction time (Table 3). The Illinois No. 6 coal consumes slightly more hydrogen at long reaction times. This method is in error probably by about 3-5% of naphthalene yield since some tetralin becomes chemically bonded to fractions of the coal. It is further noted that the yields of 1-methylindan are only slightly greater at longer reaction times for Illinois No. 6.

It is clear from these results that the degree of oxidation of tetralin at short reaction times is similar for the two coals and that both coals undergo label exchange with the coal, reminiscent of the results of Skowronski, Heredy and Ratto.⁴ The dramatic increase in scrambling rates induced by Illinois No. 6 coal at equal degrees of oxidation of the tetralin almost certainly indicates a different scrambling mechanism than that occurring with Kaiparowitz Coal.

In the conventional picture of coal dissolution, unimolecular cleavage of weaker C-C, C-S and C-O bonds in the coal leads to free radicals (eq. 1) which abstract hydrogen from the coal or donor solvent, or undergo disproportionation, combination, fragmentation and addition reactions, and participate in chain decompositions of hydrocarbons.



Ignoring the participation of phenolic or sulfur groups in the coal for the moment, the formation of 2-tetralyl and its subsequent reaction with the solvent (eq. 2) will lead to deuterium label in the 2-position. We have demonstrated⁵ in a study of high temperature reactions of tetralyl and indanyl methyl radicals that the 1-methylindan observed in the reactions of

coal and tetralin is a product of the reverse 1,2-aryl migration of 2-tetralyl radical (eq. 3).



This reaction is endothermic with an activation barrier of 22 ± 2 kcal/mole.⁵ The presence of 1-methylindan in coal reactions indicates that coal derived radicals are sufficiently non-selective to produce 2- as well as 1-tetralyl radicals.³ A second pathway of scrambling is the reverse of eq. 2. Reaction (2f) proceeds with $\Delta G = 0.1$ kcal/mole and $\Delta H = -16.1$ kcal/mole at 427°C , from thermochemical estimates of thermodynamic properties of 1- and 2-tetralyl radicals.⁶ Thus, although the reaction is slow, equal concentrations of 1- and 2-tetralyl radical would exist at equilibrium at 427°C . The direct unimolecular interconversion of 1-tetralyl and 2-tetralyl radicals is predicted not to occur due to the net antibonding configuration of the 1,2-hydrogen atom shift intermediate.⁷ Of course, 1,2-hydrogen shifts and alkyl shifts in carbonium ions proceed through a net bonding intermediate and occur very rapidly.

Thus, constituents of the coal which could convert radicals (which undergo relatively inefficient bimolecular interconversion) to carbonium ions (which undergo very rapid unimolecular rearrangements), would cause significant enhancements in scrambling rates. A likely candidate for the conversion of radicals to carbonium ions is the pyrite in Illinois No. 6 coal. Illinois No. 6 contains about 3% sulfur, two-thirds of which is associated with iron. By contrast, the low-sulfur Kaiparowitz contains only 40 ppm of iron. Reaction of Fe^{3+} with solvent radicals may lead to the corresponding carbonium ions



which would rapidly equilibrate the 1- and 2-hydrogens of tetralin. Consistent with this view, Bockrath has observed an enhanced rate of isomerization of tetralin to 1-methylindan with added pyrite.⁹ Whitehurst, et al, have observed that pyrite catalyzes solvent isomerization, dehydrogenation, and hydrogen transfer, though pyrite is by no means the only active catalytic agent.¹⁰ The Fe_3 form of iron is not specified in eq. 4. The oxidation of radicals by Fe^{3+} in aqueous media is well known.¹¹ However, more work is needed to identify the structure and mechanisms of the iron sulfide participation in

nonpolar donor media. Further work is underway in this laboratory to identify the structural features of coals which enhance hydrogen shuttling.

REFERENCES

- (1) James A. Franz, Prepr. Fuel Div. Amer. Chem. Soc. 24 (2), 263 (1979).
- (2) James A. Franz, Fuel, 58:405 (1979).
- (3) James A. Franz and Donald M. Camaioni, Fuel, in press.
- (4) R. P. Skowronski, L. A. Heredy, and J. J. Ratto, Prepr. Fuel Div., Amer. Chem. Soc., 23 (4), 115 (1979).
- (5) James A. Franz and Donald M. Camaioni, J. Org. Chem., in press, to appear February 1981.
- (6) Sidney W. Benson, "Thermochemical Kinetics Methods for the Estimation of Thermochemical Data and Rate Parameters," John Wiley & Sons, New York, N.Y., 1968 and H. Edward O'Neal and Sidney W. Benson in "Free Radicals" Ed. Jay K. Kochi, Volume I, pp 275-359, Wiley-Interscience, New York, N.Y..
- (7) James A. Wilt in ibid., pp 334-501.
- (8) Jerry March, "Advanced Organic Chemistry" 2nd Ed.,, Chs. 5, 18, McGraw Hill Book Co., New York, N.Y. 1977.
- (9) B. Bockrath, private communication.
- (10) D. D. Whitehurst, T. O. Mitchell, M. Farcasiu and J. J. Dickert, Jr., "The Nature and Origin of Asphaltenes in Processed Coals. Vol. 1. The Chemistry and Mechanisms of Coal Conversion to Clean Fuel," Electric Power Research Institute Report AF-1298, Volume 1, Research Project 410, December 1979, p I-66.
- (11) Cheves Walling, Acc. Chem. Res. 8, 125 (1975).

TABLE 1.

DEUTERIUM LABEL DISTRIBUTIONS IN RECOVERED TETRALIN AND NAPHTHALENE

Coal	Reaction Time	Tetralin ^a			Naphthalene ^b	
		Arom	1	2	1	2
Illinois No. 6	0	0	100	0	--	--
	2.5	5.6	91.8	2.5	91.3	8.7
	5.0	30.0	55.2	0.8	78.3	21.7
	10.0	29.9	51.7	18.4	74.6	25.4
	35.0	35.7	39.3	25.0	54.8	45.2
	60.0	36.6	38.8	24.6	59.1	40.8
Kaiparowitz	0	0	100	0	--	--
	10	2.5	95.4	2.1	45.1	4.9
	35	4.2	90.2	5.6	92.0	8.0
	60	10.9	78.2	10.9	87.5	12.5

^a % of deuterium in the aromatic, 1-, or 2-position

^b % of deuterium in the 1- or 2-position

TABLE 2

ISOTOPE DEPLETION IN RECOVERED TETRALIN

Coal	Reaction Time, min	Deuterium Atoms/Molecule ^a
Illinois No. 6	0	2.0
	2.5	1.88
	5.0	1.64 ^b
	10.0	1.22 ^b
	35.0	1.68
	60.0	1.45
Kaiparowitz	0	2.0
	10	1.82
	35	1.56
	60	1.52

^a ± 0.2 Atoms/molecule

^b This point is suspect due to a possible temperature error during the reaction.

TABLE 3

RECOVERED YIELDS OF TETRALIN, 1-METHYLINDAN AND NAPHTHALENE
AND HYDROGEN UPTAKE PER CARBON IN COAL^a

Coal	Reaction Time, min	Tetralin	1-methylindan	Naphthalene	H uptake, Atoms/Carbon Atom of Coal ^b
Illinois No.6	2.5	89.7	0.2	10.1	0.12
	5.0	86.3	0.3	13.4	0.17
	35	63.0	2.4	34.6	0.43
	60	51.9	3.5	44.6	0.55
Kaiparowitz	2.5	90.6	0.2	9.2	0.12
	5.0	86.1	0.3	13.5	0.17
	10	79.9	0.2	19.9	0.26
	25	72.7	1.9	26.8	0.34
	60	62.5	2.9	34.6	0.44

^a Yields of tetralin, 1-methylindan and naphthalene are normalized to 100%

^b Uses the yield of naphthalene recovered to estimate hydrogen uptake, neglects naphthalene and tetralin bound to coal products (~ 3%).

AN ISOTOPIC INVESTIGATION OF THE CHEMISTRY OF COAL HYDROLIQUEFACTION

L. A. Heredy, R. P. Skowronski

J. J. Ratto, I. B. Goldberg

Energy Systems Group
Rockwell International Corporation
8900 De Soto Avenue
Canoga Park, California 91304

Science Center
Rockwell International Corporation
1049 Camino Dos Rios
Thousand Oaks, California 91360

I. INTRODUCTION

We reported earlier on a deuterium tracer method for investigating the mechanisms of coal liquefaction.⁽¹⁻³⁾ The research involved the use of deuterium gas,⁽¹⁾ or deuterium gas and tetralin-d₁₂^(2,3) for hydrogenation, and the use of the deuterium as an isotopic tracer to follow the incorporation of hydrogen into the coal. After separation of the liquefaction products, the product fractions were analyzed for deuterium incorporation into different structural positions. It was found that when deuterium alone was used (without donor solvent) for liquefaction, the deuterium content of the products increased in the following order: oil < asphaltene < preasphaltene < residue. When deuterium and tetralin-d₁₂ were used, the deuterium contents of the product fractions were about the same. In both types of experiments, preferential incorporation of deuterium was found in the benzylic structural positions of each fraction. Similarly, preferential incorporation of protium was observed in the benzylic position of the recovered tetralin-d₁₂.

A number of related investigations have been reported on the use of deuterium as a tracer in coal hydrogenation research. Schweighardt, et al.⁽⁴⁾ examined a centrifuged liquid product from a Synthoil run after heating it to 450°C with deuterium gas; Kershaw and Barrass⁽⁵⁾ reported on the examination of products from the reaction of coal with deuterium gas using SnCl₂ as catalyst; Franz⁽⁶⁾ investigated the products from the reaction of a subbituminous coal with tetralin-1,1-d₂ at 427°C and 500°C; Cronauer, et al.⁽⁷⁾ reported on the interaction of deuterium-labeled tetralin with coal model compounds; King and Stock⁽⁸⁾ investigated the influence of coal and coal-related compounds on the exchange reaction between diphenylmethane and perdeuteriotetralin.

This paper presents the results of experiments which were conducted to investigate the respective roles of gas-phase and donor-solvent hydrogen in coal hydroliquefaction. Coal hydrogenation experiments were carried out with ²H₂/tetralin-h₁₂ and ¹H₂/tetralin-d₁₂ mixtures and tetralin-d₁₂ under N₂ pressure to study the mechanisms that are in operation.

II. EXPERIMENTAL

A. MATERIALS

A high-volatile A bituminous coal (80.1% C, 5.1% H, 1.6% N, 3.6% S, 9.6% O, by weight, daf basis, 7.7% ash) from the Loveridge Mine, Pittsburgh Seam was used. The coal was stored under nitrogen, ground to -200 mesh, and dried in vacuo for 4 hr at 115°C before use in each experiment. Technical-grade deuterium (>98 atom % deuterium, typical HD:0.5%) and high-purity nitrogen were utilized. Some of the tetralin-d₁₂ was prepared in our laboratories⁽³⁾, and some was purchased from the Aldrich Chemical Co., Inc. The isotopic purity of both materials was >99 atom % deuterium. The isotopic purity of tetralin-d₁₂ was determined by proton-NMR using p-dioxane as an internal reference.

B. EXPERIMENTAL AND ANALYTICAL PROCEDURES

A schematic outline of the experimental and analytical procedures is shown in Figure 1. Batch experiments were performed using a 1-liter stirred Autoclave Engineer's autoclave equipped with a coal injection system. In a typical experiment, the autoclave was charged with 25 g of tetralin, heated, and 25 g of coal was injected at temperature with the appropriate cover gas. After the scheduled reaction time had elapsed, the furnace was lowered from the autoclave, and the external surface was air-cooled. Also, water was circulated through the autoclave's internal cooling coils. After the autoclave had cooled to ambient temperature, the gas volume was measured using a wet test meter, and product gas samples were analyzed by GC-MS. The solvent was distilled from the product mixture and analyzed by NMR and GC-MS. The solid and liquid products were solvent fractionated into oil (hexane soluble, benzene soluble), asphaltene (hexane insoluble, benzene soluble), preasphaltene (THF soluble, benzene insoluble), and residue (THF insoluble) fractions. A portion of each fraction was combusted and its protium/deuterium ratio was determined by MS analysis of the resulting water. Each fraction was analyzed to determine its elemental composition. The fractions also were analyzed by proton and deuteron NMR spectrometry.

Proton NMR and deuteron NMR, spectra of soluble fractions, and recovered solvent mixtures were obtained by using a JEOL FX60Q FT NMR spectrometer. A flip angle of 45° was used which corresponds to $14 \mu\text{s}$ for ^1H and $75 \mu\text{s}$ for ^2H . The pulse repetition times were 6.0 and 9.0 s, respectively. Chloroform-d was used as the ^1H NMR solvent, and chloroform was used as the ^2H NMR solvent. Integrations were obtained using software supplied by JEOL, Inc. The GC-MS analyses were conducted by Shrader Analytical Laboratories, Inc., using a Pye-Unicam Model 105 chromatograph interfaced to an AEI Model MS-30 mass spectrometer.

III. RESULTS AND DISCUSSION

Three experiments were conducted to explore the roles of gas-phase and donor-solvent hydrogen on coal liquefaction. Tetralin- h_{12} , tetralin- d_{12} under $^2\text{H}_2$ or $^1\text{H}_2$, or N_2 pressure were used, as shown in the experimental matrix (Table 1). In each experiment, there was only one source of deuterium atoms: deuterium gas in Experiment 120 and tetralin- d_{12} in Experiments 121 and 122. In Experiment 122, nitrogen cover gas was used to eliminate those reaction pathways which involve gas-phase hydrogen.

TABLE 1
EXPERIMENTAL MATRIX FOR DONOR SOLVENT HYDROGENATION EXPERIMENTS

Experiment*	Coal +				
	Gas			Solvent	
	Protium	Deuterium	Nitrogen	Tetralin- h_{12}	Tetralin- d_{12}
D/P		X		X	
P/D	X				X
N/D			X		X

*Experiment name indicates gas isotopic composition/solvent isotopic composition (i.e., D/P refers to deuterium gas/tetralin- h_{12}).

A. PRODUCT YIELDS AND COMPOSITIONS

The product yields are shown in Table 2. It should be noted that the asphaltene and preasphaltene yields are lower than would be expected at 425°C and 15 MPa, particularly for the experiment in which nitrogen was the cover gas. We believe that this resulted from using unfavorably small amounts of reactants for the 1-liter autoclave to minimize the use of expensive tetralin-d₁₂. Nevertheless, previous coal hydrogenation experiments⁽²⁾ conducted with deuterium gas and tetralin-d₁₂ in a 1-liter and in a 250-ml autoclave showed that while higher soluble product yields were obtained in the smaller autoclave, the isotopic incorporation patterns were similar in both experiments.

TABLE 2
PRODUCT YIELDS FROM DONOR SOLVENT
HYDROGENATION EXPERIMENTS
(wt %)

Product	Experiment		
	D/P	P/D	N/D
Gas	10	11	9
Oil	24	19	16
Asphaltenes	8	4	1
Preasphaltenes	7	3	3
Residue	51	63	71

The deuterium contents of the product fractions are shown in Table 3. The deuterium content of the heavier fractions (asphaltenes, preasphaltenes, and residue) depend principally on the isotopic composition of the gas phase. These fractions have high atom % deuterium content in Experiment D/P, where ²H₂ gas and tetralin-h₁₂ were used, and low atom % deuterium content in Experiment P/D, where ¹H₂ gas and tetralin-d₁₂ were used. The atom % deuterium content of the heavy fractions is between these two extreme values in Experiment N/D where tetralin-d₁₂ was used under N₂ pressure. This indicates that the use of the inert gas, which precludes reactions with molecular hydrogen, allows pathways which are otherwise less significant to become more important in the reaction sequence. No obvious trend regarding the deuterium content was observed for the gas and oil fractions.

B. PRODUCT GAS COMPOSITIONS

The gas compositions, determined by gas chromatographic analysis, are shown in Table 4. The isotopic compositions of the product gases were determined by GC-MS analysis. The isotopic compositions of methane, ethane, and propane are shown in Table 5. The main results are summarized below:

- 1) The concentrations of the D₀ species can be correlated with the deuterium source used in the experiment. The D₀ species can form from the corresponding radicals by protium abstraction from the coal in any experiment, from the protium gas (Run P/D), or from tetralin-h₁₂ (Run D/P). The amount of D₀ species is reduced if the same radicals abstract deuterium from the tetralin-d₁₂ (Runs P/D and N/D) or ²H₂ gas (Run D/P). It appears that ²H₂ gas reacts more

TABLE 3
DEUTERIUM CONTENTS OF PRODUCTS
(Atom % of Total Hydrogen)

Product	Experiment		
	D/P	P/D	N/D
Gas	29	33	29
Oil	26	26	12
Asphaltenes	42	21	31
Preasphaltenes	34	15	28
Residue	<u>46</u>	<u>20</u>	<u>36</u>
Total Product	32	27	28

TABLE 4
PRODUCT GAS COMPOSITIONS
(Weight in Grams*)

Component	Experiment		
	D/P	P/D	N/D
CH ₄	1.10	1.36	0.94
C ₂ H ₄	0.01	0.01	0.01
C ₂ H ₆	0.58	0.63	0.43
C ₃ H ₆	0.01	0.01	0.01
C ₃ H ₈	0.35	0.35	0.24
i-C ₄ H ₁₀	0.01	0.03	0.05
n-C ₄ H ₁₀	0.08	0.10	0.08
i-C ₅ H ₁₂	0.02	0.01	-
n-C ₅ H ₁₂	0.02	0.02	0.02
CO	0.09	0.09	0.05
CO ₂	0.10	0.10	0.22
H ₂ S	<u>0.01</u>	<u>0.08</u>	<u>0.07</u>
Total	2.38	2.79	2.12

*Weights calculated on an all-protium basis

TABLE 5
ISOTOPIC COMPOSITIONS OF THE PRODUCT GASES
(%)

Component (Experiment)	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈
<u>CH₄</u>									
D/P	28	29	30	13	0	-	-	-	-
P/D	36	25	13	14	12	-	-	-	-
N/D	40	24	14	11	11	-	-	-	-
<u>C₂H₆</u>									
D/P	8	31	32	19	10	0	0	-	-
P/D	23	17	19	15	10	10	6	-	-
N/D	*	*	*	11	9	12	13	-	-
<u>C₃H₈</u>									
D/P	27	24	17	10	10	6	4	2	0
P/D	35	31	16	7	3	2	3	2	1
N/D	36	27	14	9	3	4	5	2	2

*Interference from other species causes uncertainty in these values.

effectively with the radicals than tetralin-d₁₂ does.* This tentative conclusion is supported by previous experimental data⁽³⁾ obtained on the hydrogenation of coal with deuterium gas at 380°C without added donor solvent. The D₀ components in that experiment were for CH₄:3%, for C₂H₆:0%, and for C₃H₈:12%, which shows that the ²H₂ gas is a more effective deuterium source for the conversion of methyl, ethyl, and propyl radicals to the corresponding deuterated hydrocarbons than is tetralin-d₁₂. Hydrogen exchange with the solvent probably contributes to a lesser extent to the formation of these species, because even by the end of the experiment no more than one-third of the solvent hydrogen in any position has been exchanged. This may be due to the greater access of the hydrogen gas molecules to the pore structure of the coal compared with that of the solvent molecules.

- 2) Only minor differences were observed between the isotopic compositions of the gas products of the tetralin-d₁₂ run made with N₂ cover gas in one case (Run N/D) and under ¹H₂ pressure in the other (Run P/D). These results show that very little isotopic exchange takes place in the gas phase between hydrogen and hydrocarbons.
- 3) Fully deuterated methane and ethane were detected only in those experiments in which tetralin-d₁₂ was used. No such species were found in Experiment D/P, where tetralin-h₁₂ was used, and the deuterium source was ²H₂. This indicates that the CD₄ and C₂D₆ species were formed from the tetralin-d₁₂ only. It also appears that at least some of the CD₄ and C₂D₆ were formed from the solvent prior to the injection of the coal. Additional investigations are in progress to clarify this point.

*Alternately, isotopic exchange reactions may occur with the radical precursors.

C. COMPOSITION OF THE RECOVERED SOLVENT

1. GC-MS Analyses

The GC-MS analyses of the recovered solvents are shown in Table 6. In Experiment D/P, tetralin- h_{12} was used and the source of deuterium was 2H_2 gas. The isotopic distributions in the recovered tetralin and naphthalene are very similar. In both compounds, D_1 and D_2 species predominate, but sizable concentrations of D_3 and D_4 species are also present. The predominance of the D_1 and D_2 species, coupled with information from the NMR analysis of the solvent (Table 7), which show that 76% of the incorporated deuterium is in the α -aliphatic position, indicates that the α -tetralinyl radical has a significant role in the transfer of deuterium from the gas phase into the coal.

TABLE 6
ISOTOPIC DISTRIBUTIONS IN TETRALIN AND NAPHTHALENE
IN THE RECOVERED SOLVENTS
(%)

Component (Experiment)	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}
<u>Tetralin</u>													
D/P	28	32	22	11	5	1	1	0	0	0	0	0	0
P/D	1	1	3	3	4	3	3	4	6	11	21	23	17
N/D	1	1	2	3	3	2	3	1	4	9	23	30	18
<u>Naphthalene</u>													
D/P	30	32	21	10	4	2	1	0	0	-	-	-	-
P/D	4	6	7	11	14	20	18	13	7	-	-	-	-
N/D	1	2	4	7	11	17	21	22	15	-	-	-	-

TABLE 7
ISOTOPIC COMPOSITION OF THE RECOVERED TETRALIN

Experiment	Incorporated Isotope	Atom % Isotope	Isotope Distribution (%)		
			H_{ar}	H_{α}	H_{β}
D/P	2H	13.5	10	76	14
P/D	1H	23.4	8	75	17
N/D	1H	18.6	9	74	17

The data from Experiment D/P also indicate that there is direct incorporation of deuterium gas into the coal. At the end of Experiment D/P there was only 13.5% deuterium in the tetralin. The α -aliphatic position of tetralin contained 31% deuterium ($13.5 \times 0.76 \times 3$) at the end of the experiment. Nevertheless, some of the coal products (asphaltene, preasphaltene, and residue), which formed throughout

the duration of the reaction, contained considerably more deuterium. This large amount of deuterium incorporation into the coal products strongly indicates that there is also a direct route for deuterium incorporation into the coal without the participation of tetralin.

In Experiments P/D and N/D, tetralin- d_{12} was used. The following observations can be made regarding these experiments:

- 1) In these experiments, the D_{11} and D_{10} (that is, H_1 and H_2) species predominate in the recovered tetralin. This is similar to Experiment D/P, in which the D_1 and D_2 species predominate. The predominance of the D_{11} and D_{10} species, together with the NMR analysis of the solvent indicating that 74-75% of the incorporated protium is in the α -position (Table 7), indicates that the α -tetralinyl radical has an important role in the hydrogen transfer. This is true for hydrogen transfer from the gas phase into the coal (Experiment P/D) as well as for hydrogen transfer from one site in the coal structure to another (Experiment N/D).
- 2) In contrast to Experiment D/P, where no species containing more than six deuterium atoms were detected, species with fully exchanged hydrogen (D_0) were found in each experiment. The extent of isotopic exchange was greater in these experiments because in contrast to Experiment D/P, isotopic exchange between the coal and the donor solvent could take place.
- 3) There is only a small difference between the isotopic distribution of the recovered tetralin obtained in Run P/D on the one hand, and Run N/D on the other. This indicates that the extent of isotopic exchange between the coal and the solvent is greater than it is between the hydrogen gas and the solvent. This same result is further substantiated by the data shown in Table 7.
- 4) The isotopic distribution found in the naphthalene is similar to that observed in the tetralin in Experiment N/D in that the least exchanged species (D_4 - D_8) are predominant. The isotopic distribution of the recovered naphthalene from Experiment P/D shows relatively large values for each of the species of low deuteration (D_0 through D_4), which indicates that a significant amount of the gas-phase protium exchanged with the naphthalene.

2. NMR Analyses

The recovered solvents were analyzed by proton and deuterium NMR spectroscopy. As an example, the deuterium NMR spectrum of the recovered solvent from Experiment D/P is shown in Figure 2. The tetralin α -aliphatic and β -aliphatic absorptions are shown at 1.8 ppm and 2.8 ppm, and the aromatic absorption of tetralin at 7.1 ppm. The aromatic absorptions at 7.4 and 7.8 ppm correspond to the β - and α -positions in naphthalene. There are additional absorptions in the spectrum (at 0.9, 1.3, 2.3, and 6.9 ppm) corresponding to deuterated alkylbenzenes, indan, methylindan, and cis- and trans-decalins, which form in small amounts during the reactions.

The isotopic composition data of the recovered tetralin, as determined by NMR analysis, are shown in Table 7. In Experiment D/P where tetralin- h_{12} and deuterium gas were used, 13.5 atom % deuterium was found in the recovered tetralin. In the other experiments, where fully deuterated tetralin was used, the protium incorporation ranged from 18.6% to 23.4%. The amount was larger in the tetralin from the experiment with the protium atmosphere (P/D) than from the experiment with the nitrogen atmosphere (N/D)--23.4 versus 18.6 atom % 1H .

The distribution of the incorporated isotope among the three structurally different sites in the solvent was nearly identical in each experiment. Approximately 75% was incorporated in the α -aliphatic position, 16% in the β -aliphatic, and 9% in the aromatic position. These proportions did not change significantly regardless of whether the reaction was conducted under protium or nitrogen pressure. The N/D system was also tested using reaction times of 1/4 and 1/2 hour. It was found⁽⁹⁾ that the extent of isotopic exchange with the solvent increases with time; however, the ratio of exchanged hydrogen in the three different structural positions of the solvent remains constant within this reaction time range (1/4 to 1 hour).

The following conclusions have been drawn from these measurements: (1) the relative reactivities of the α -aliphatic, β -aliphatic, and aromatic C-H bonds of tetralin at 425°C for ^1H - ^2H isotopic exchange between tetralin and coal are: 75:16:9; (2) these ratios do not change significantly regardless of whether N_2 or $^1\text{H}_2$ cover gas or whether tetralin- d_{12} / $^1\text{H}_2$ or tetralin- h_{12} / $^2\text{H}_2$ reactant combinations are used.

ACKNOWLEDGEMENT

This work was conducted by Rockwell International for the U.S. Department of Energy under Contract DE-AC22-77ET11418.

REFERENCES

1. R. P. Skowronski, L. A. Heredy, and J. J. Ratto, Preprints ACS Div. Fuel Chem. 23 (4) 155 (1978)
2. J. J. Ratto, L. A. Heredy, and R. P. Skowronski, Preprints ACS Div. Fuel Chem. 24 (2) 155 (1979); submitted for publication in ACS Symposium Series (1980)
3. a. R. P. Skowronski, J. J. Ratto, and L. A. Heredy, Annual Technical Progress Report to DOE, FE-2328-13 (1978)
b. R. P. Skowronski, J. J. Ratto, I. B. Goldberg, and L. A. Heredy, Quarterly Technical Progress Reports to DOE, FE-2781-5 and FE-2781-6 (1980)
4. F. K. Schweighardt, B. C. Bockrath, R. A. Friedel, and H. L. Retcofsky, Anal. Chem. 48 (8) 1254 (1976)
5. J. R. Kershaw and G. Barrass, Fuel 56 (4) 455 (1977)
6. J. A. Franz, Fuel 58 (6) 405 (1979)
7. D. C. Cronauer, D. M. Jewell, Y. T. Shah, and R. J. Modi, Ind. Eng. Chem. Fundam. 18 (2) 153 (1979)
8. H. H. King and L. M. Stock, Fuel 59 447 (1980)
9. R. P. Skowronski, et al., unpublished data

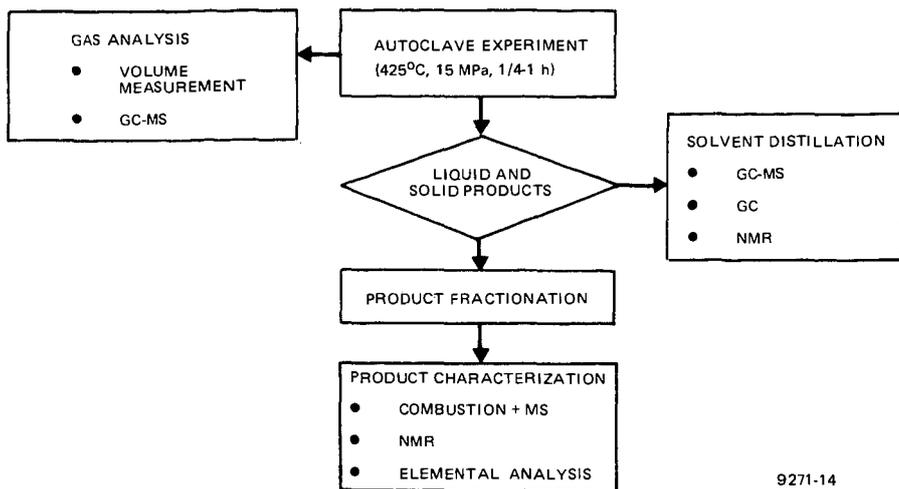


Figure 1. Experimental Procedure

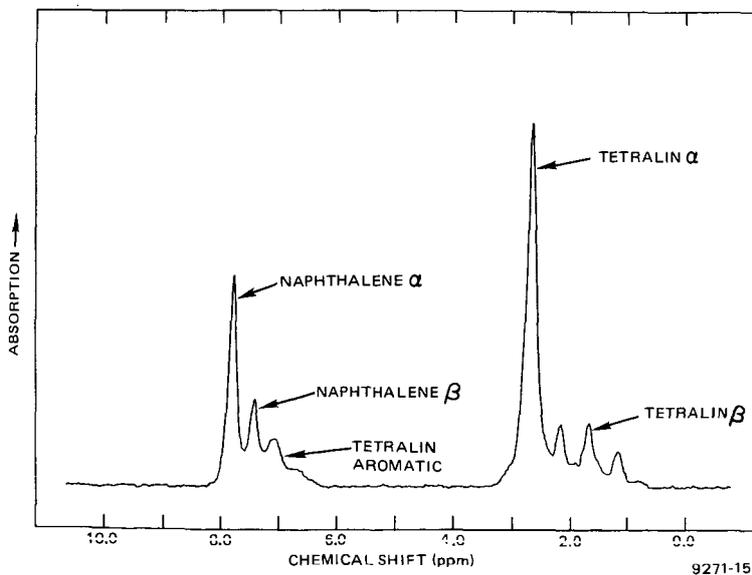


Figure 2. Deuteron NMR Spectrum of Recovered Solvent from Experiment D/P

MODEL PATHWAYS FOR HYDROGEN TRANSFER IN COAL LIQUEFACTION

P.S.Virk, D.H.Bass, and M.J.Garry,

Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Hydrogen transfer from donor solvents to coal during liquefaction has been modelled by reactions between selected pure substrates. Model donors used were tetralin (control), Δ^1 - and Δ^2 -dialins, cyclohexanol and o-cyclohexylphenol, while anthracene and phenanthrene served as model acceptors. Experiments over the temperature range 250-450 C, at times from 0.1-10.0 hr, and donor/acceptor ratios of 0.12-16, revealed that, in general, three types of reactions occurred. In order of importance these were: (R1), the desired hydrogen transfer from donor to acceptor, (R2), the reversion of hydrogenated acceptor to original acceptor, either by elimination of molecular hydrogen or by disproportionation, and (R3), donor decomposition. Kinetic data showed that for every donor-acceptor pair (R1) was bimolecular, being of order one in each substrate. Also, Arrhenius parameters in all cases yielded activation entropies $\Delta S^\ddagger \sim -30$ eu, indicative of a tight transition state. These accord with our earlier suggestion that the mechanism of hydrogen transfer might involve concerted pericyclic group-transfer reactions that are thermally-allowed by the Woodward-Hoffmann rules for orbital symmetry conservation. Detailed kinetic data were also obtained for each of (R2) and (R3), permitting fairly complete description of the present model pathways for hydrogen transfer.

PARTICIPATION OF HYDROGEN IN THE HYDROGENOLYSIS AND HYDROGENATION
OF COAL-RELATED MODEL COMPOUNDS CATALYZED BY ZINC HALIDES

T. J. Fredrick and A. T. Bell

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemical Engineering
University of California, Berkeley, CA 94720

INTRODUCTION

Model compound studies have recently been performed to help elucidate the types of reactions which occur during the liquefaction of coal in presence of $ZnCl_2(1-5)$. These investigations have shown that $ZnCl_2$ will catalyze the cleavage of ether, sulfide, and aliphatic bridges between aromatic centers and the hydrogenation of fused ring aromatics. It has also been demonstrated that the reactivity of a given structure can be strongly affected by the composition of substituents present on the aromatic nuclei. The purposes of the present work were to identify the role of molecular hydrogen in the hydrogenolysis and hydrogenation of coal-related model compounds and to demonstrate the differences in the ability of $ZnCl_2$, $ZnBr_2$, and ZnI_2 to activate H_2 .

EXPERIMENTAL

Apparatus

Reactions were carried out in a 300-cm³ stirred, stainless-steel autoclave fitted with a glass liner to facilitate introduction of reactants and removal of products. The pressure and temperature within the autoclave were monitored continuously. For most of the experiments described in this paper, the solvent and catalyst were preheated to reaction temperature within the autoclave. The reactant, dissolved in a small amount of solvent, was then injected into the autoclave from a small pressure vessel. Samples of the liquid products were withdrawn at prescribed times during the course of a run.

Materials

Model compounds were obtained commercially. These materials were dried but not purified before use. Benzene and cyclohexane, used as solvents, were dried by refluxing over a sodium-benzophenone mixture and then distilled under dry N_2 .

The $ZnCl_2$, $ZnBr_2$ and ZnI_2 were dried in a vacuum oven overnight at 105°C and then stored in an N_2 -purged dry box. Weighing of the catalyst and transfer into the glass liner was also carried out in the dry box.

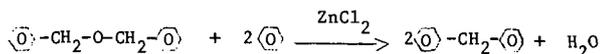
Product Analysis

The liquid products were analyzed by gas chromatography. Product identification was established by gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

Cleavage of Ether Linkages

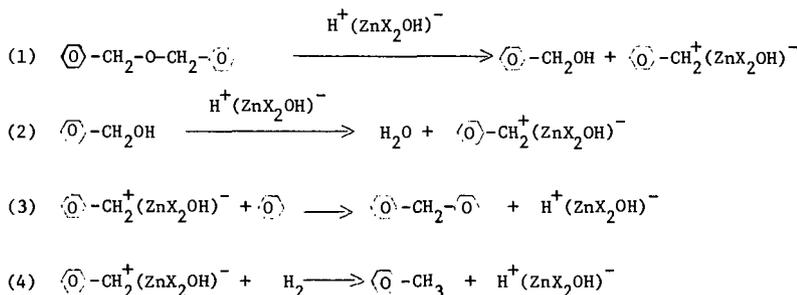
The effects of hydrogen partial pressure and catalyst composition on the hydrogenolysis of dibenzyl ether in benzene solution are listed in Table I. It is observed that in the presence of $ZnCl_2$, diphenyl methane is the principal product formed and that the extent of reaction is unaffected by the presence or absence of molecular hydrogen. These results indicate that the overall reaction can be written as follows:



and that the hydrogen required for the formation of water derives from the benzene. As a result, molecular hydrogen does not appear to be essential for the progress of the reaction.

Table I shows that the catalytic activity of zinc halides decreases in the order $ZnCl_2 > ZnBr_2 > ZnI_2$. It is also seen that in the presence of $ZnBr_2$ and ZnI_2 , toluene is produced in addition to diphenyl methane. Moreover, while the extent of dibenzyl ether conversion is unaffected by the partial pressure of H_2 , the selectivity to toluene increases in direct proportion to the H_2 partial pressure. These results suggest that $ZnBr_2$ and in particular ZnI_2 are more effective in activating H_2 than $ZnCl_2$, but that even in an activated state hydrogen does not affect the rate of consumption of dibenzyl ether. However, once activated hydrogen becomes effective in the formation of toluene.

The accumulated evidence suggests that the hydrogenolysis of dibenzyl ether may proceed via the following sequence of steps

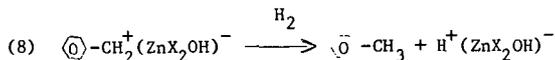
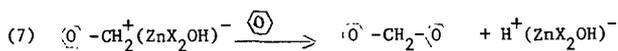
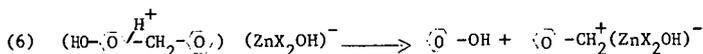
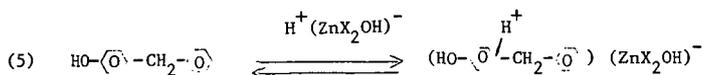


Studies in which the ratio of H_2O to ZnX_2 were varied clearly demonstrate that the active form of the catalyst is a Brønsted acid, $H^+(ZnX_2OH)^-$. Cleavage of the ether is initiated by protonation of the ether and the rate of this reaction is affected by the composition of the zinc halide. The nature of the final reaction products is dictated by reactions 3 and 4 and the ratio of the rate coefficients associated with these reactions is determined by the catalyst composition.

Cleavage of Aliphatic Linkages

The hydrogenolysis of 4-hydroxydiphenyl methane (4HDM) and 1-benzyl-naphthalene (1BN) in benzene solution were studied to establish the effects of hydrogen partial pressure and catalyst composition on the cleavage of aliphatic linkages between aromatic nuclei. In the presence of zinc halide catalyst, 4HDM reacts to form phenol, diphenyl methane, and toluene. As shown in Table II, the hydrogen partial pressure has no effect on the conversion of 4HDM but the selectivity to toluene increases with the hydrogen partial pressure. The catalytic activity in this instance decreases in the order $ZnBr_2 > ZnCl_2 > ZnI_2$, and the selectivity to toluene increases in the order $ZnBr_2 > ZnCl_2 > ZnI_2$. The reaction of 1BN produces naphthalene, diphenyl methane and toluene. The effects of hydrogen partial pressure and catalyst composition on the reactions of this compound are similar to those for 4HDM.

The reaction products obtained from 4HDM and 1BN and the kinetics by which these reactants are converted to products (2) can be explained on the basis of the following mechanism:

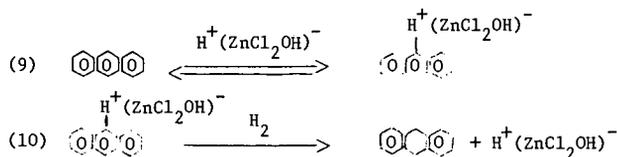


As in the case of the cleavage of ether linkages, reaction is initiated by protonation of the reactant. The primary difference is that this step is reversible and cleavage of the aliphatic linkages occurs in a subsequent rate limiting 1 step. The distribution of final products is governed by reactions 7 and 8.

Hydrogenation of Condensed Aromatics

Studies of the hydrogenation of fused-ring aromatics catalyzed by $ZnCl_2$ have shown (5) that 1-naphthol and anthracene undergo extensive reaction. The influence of hydrogen partial pressure on the extent of reaction and the distribution of products formed is shown in Table III. It is apparent that in the absence of hydrogen both reactants are converted extensively to tar via Scholl condensation. In the presence of hydrogen, 1-naphthol is hydrogenated to 1,2,3,4-tetrahydro-1-naphthol which then undergoes dehydration to form dihydronaphthalene. The latter compound is very reactive (5), undergoing hydrogenation to form tetralin and dehydrogenation to form naphthalene. The hydrogenation of anthracene produces primarily dihydroanthracene and smaller amounts of tetrahydroanthracene and octahydroanthracene.

The hydrogenation of both reactants is believed to proceed by sequential protonation and hydride addition, as exemplified by the first stages of anthracene hydrogenation shown below.



The formation of tetrahydro- and octahydroanthracene is assumed to involve a repetition of steps similar to reactions 9 and 10.

CONCLUSIONS

The following conclusions may be drawn from the present study:

- Zinc halide catalysts are active in their Bronsted acid form, e.g., $\text{H}^+(\text{ZnX}_2\text{OH})^-$.
- Cleavage of ether and aliphatic linkages between aromatic nuclei is indicated by protonation of the substrate and is unaffected by the presence of molecular hydrogen.
- Hydrogen transfer to benzylic groups liberated by the cleavage of dibenzyl ether, 4HDM and LBN and the selectivity for forming toluene from these reactants depends on the nature of the halide used.
- The hydrogenation of fused-ring aromatics involves molecular hydrogen and appears to proceed via sequential protonation and hydride transfer.

REFERENCES

1. D. P. Mobley and A. T. Bell, Fuel 58, 661 (1979).
2. N. D. Taylor and A. T. Bell, Fuel 59, 499 (1980).
3. D. P. Mobley and A. T. Bell, Fuel 59, 499 (1980).
4. D. P. Mobley and A. T. Bell, J. Cat. 64, 494 (1980).
5. S. S. Salim, Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley, CA, 1980.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

Table I. Effects of H₂ Pressure and Catalyst Composition on the Reaction of Dibenzyl Ether

Catalyst	H ₂ Press. (atm) ^a	Ether Conversion (%) ^b	Toluene	Product Yield ^c (%) Diphenyl Methane	Other
ZnCl ₂	35(N ₂)	81.3	0	88.0	10.2
ZnCl ₂	34	84.5	0	88.4	12.7
ZnCl ₂	82	79.0	0	88.4	9.1
ZnBr ₂	34	22.2	1.8	55.5	45.0
ZnI ₂	31	12.0	9.2	45.6	61.0
ZnI ₂	82	6.0	30.2	31.3	42.2

Reaction conditions: T = 225°C; Benzene = 80 cm³; Dibenzyl Ether ZnX₂ = 4.0 mole/mole.

^aAt reaction temperature.

^bFollowing 30 min of reaction.

^cBased on moles of dibenzyl ether reacted

^dBenzyl alcohol, benzyl halide and dibenzyl benzenes.

Table II. Effects of H₂ Pressure and Catalyst Composition on the Reactions of 4HDM and IBN

Reactant	Catalyst	H ₂ Press. (atm) ^a	Reactant Conversion (%) ^b	Toluene	Product Yield ^c (%) Diphenyl methane
4HDM	ZnCl ₂	37	27.1	5.4	38.2
4HDM	ZnCl ₂	71	27.9	10.5	30.0
4HDM	ZnBr ₂	44	62.2	3.4	42.0
4HDM	ZnI ₂	37	12.6	27.9	20.2
4HDM	ZnI ₂	68	13.7	49.9	13.7
IBN	ZnCl ₂	44	16.8	12.9	35.2
IBN	ZnCl ₂	68	17.4	20.3	31.7
IBN	ZnBr ₂	81	22.7	6.9	51.8
IBN	ZnI ₂	51	13.4	37.3	26.7

Reaction conditions: T = 325°C; Benzene = 80 cm³; 4HDM/ZnX₂ = 40 mole/mole; IBN/ZnX₂ = 1.0 mole/mole

^aAt reaction temperature.

^bFollowing 2 hr of reaction.

^cBased on moles of dibenzyl ether reacted.

Table III. Effects of Gas Composition on the Reactions of 1-Naphthol and Anthracene

Products from 1 - Naphthol	H ₂ Conversion ^a (%)	N ₂ Conversion ^a (%)
alkylbenzenes	0.1	-
tetralin	14.0	0.1
dihydronaphthalene	2.1	0.2
naphthalene	3.4	1.6
1-tetralene	3.5	1.6
1,2,3,4 -tetrahydro-1-naphthol	0.1	trace
5,6,7,8 -tetrahydro-1-naphthol	2.1	trace
2-naphthol	-	0.5
tar	-	77.0
Products from Anthracene	H ₂ Conversion ^a (%)	N ₂ Conversion ^a (%)
alkylnaphthalenes	0.4	-
octahydroanthracene	3.2	-
tetrahydroanthracene	13.0	trace
dihydroanthracene	51.0	0.9
tar	-	94.0

Reaction conditions: T = 325°C; P = 107 atm; Cyclohexane = 50 cm³; 1 - naphthol / ZnCl₂ = 1.85 mole/mole
Anthracene/ZnCl₂ = 1.85 mole/mole

^aFollowing 1 hr of reaction.

HYDROGENOLYSIS OF DILUTE SOLUTIONS OF DIBENZYL IN TOLUENE AT COAL LIQUEFACTION CONDITIONS. Lonnie W. Vernon, Exxon Research and Engineering Company, P. O. Box 4255, Baytown, Texas 77520, and Ralph Livingston and Henry Zeldes, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

Previous pyrolysis studies (L. W. Vernon, Fuel 59 102 (1980)) have shown that the conversion of dibenzyl in the presence of both tetralin and molecular hydrogen or in the presence hydrogen alone proceeds along two parallel reaction paths. Toluene is produced by a thermolysis reaction in which the rate controlling step is the thermal cleavage of the β -bond in dibenzyl. Benzene and ethyl benzene are produced by a hydrogenolysis reaction. The hydrogenolysis reaction is thought to proceed via a hydrogen atom chain carrier. ESR studies (R. Livingston, H. Zeldes, and M. S. Conradi, J. Amer. Chem. Soc. 101 4312 (1979)) have shown that benzyl is the predominant radical in the system during the pyrolysis of dilute solutions of dibenzyl in toluene. In the present study dilute solutions of dibenzyl in toluene have been pyrolyzed at 450°C, contact times of 1-3 minutes, and hydrogen pressures of 0-15 MPa. Under these conditions the conversion of dibenzyl is low (about 2-7%). The major product is benzene and the concentration of benzene increases with increasing hydrogen pressure. These results are consistent with the proposed mechanism for the conversion of dibenzyl in the presence of molecular hydrogen. In the present study, the free radical reaction is initiated by the thermolysis of dibenzyl and the benzene is produced by the hydrogenolysis of toluene via a hydrogen atom carrier.

ESR STUDY OF BIBENZYL DURING PYROLYSIS WITH AND WITHOUT HYDROGEN. Ralph Livingston and Henry Zeldes, Chemistry Division, Oak Ridge National Laboratory,* Oak Ridge, Tennessee 37830 and Lonnie W. Vernon, Exxon Research and Engineering Company, P. O. Box 4255, Baytown, Texas 77520

Free radicals have been observed during pyrolysis of bibenzyl in solution and in an earlier report (R. Livingston, H. Zeldes, and M. S. Conradi, *J. Amer. Chem. Soc.* 101, 4312 (1979)) the equilibrium $C_6H_5CH_2CH_2C_6H_5 + C_6H_5\dot{C}H_2 \rightleftharpoons C_6H_5\dot{C}HCH_2C_6H_5 + C_6H_5CH_3$ was described. The fluid sample at high pressure is circulated through a heated quartz capillary located in the ESR cavity where the contact time at pyrolytic temperature is approximately 0.5 sec. Dilute bibenzyl in toluene gives a spectrum of predominantly $C_6H_5\dot{C}H_2$, whereas in an inert solvent (benzene) $C_6H_5\dot{C}HCH_2C_6H_5$ predominates. In the present study 0.1 to 1 M bibenzyl in toluene and in benzene have been studied from 507°C to 553°C at 1300 psi. The ESR spectra have been examined to verify radical content and samples have been collected after pyrolysis for GC. Where $C_6H_5\dot{C}HCH_2C_6H_5$ predominates the usual distribution of products reported for bibenzyl (M. Poutsma, *Fuel*, 59, 335 (1980)) are seen with strong contributions from radical-radical coupling products. Where $C_6H_5\dot{C}H_2$ predominates the product distribution alters greatly and the burnup of bibenzyl falls to 1/3 to 1/7 the value in benzene solution depending on concentration and temperature. High pressure hydrogen has been injected prior to pyrolysis and substantial increases in the yields of benzene and ethylbenzene have been observed. *Research at this laboratory was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corporation.

HYDROGEN-CARBON MONOXIDE REACTIONS IN LOW-RANK COAL LIQUEFACTION

Curtis L. Knudson, Warrack G. Willson, and Gene G. Baker

U.S. Department of Energy
Grand Forks Energy Technology Center
Grand Forks, North Dakota 58202

The primary role of the gas phase in low-rank coal liquefaction appears to be the stabilization of pyrolysis products from the coal via hydrogenation and, to a much lesser extent (in a non-catalytic system), hydrogenation of coal liquids. Hydrogen donor compounds and, to a lesser extent, the bulk of the solvent perform similar functions; that is to provide another source of hydrogen in addition to that in the gas phase to quench free radicals. Solvent effects will not be discussed in this paper. Carbon monoxide and water are the favored reactants over pure hydrogen at all temperatures from 350°C to 480°C for the liquefaction of low-rank coals. The amount of carbon monoxide consumed is dependent on the quantity of coal present, indicating that the driving force is the number of reactive sites initially present in the coal.

EXPERIMENTAL

Time Sampled Batch Autoclave

Studies on batch kinetics were carried out in a 1-liter, magnetically-stirred autoclave, which is outfitted to enable the charging of a slurry to the preheated reactor and for timed sampling of the gas and slurry phase during the course of an experiment. Hot charging brings the slurry to temperature in under 3 minutes, thereby eliminating the 1- to 2-hour heat-up associated with typical autoclave operation (1,2). Alternately, the slurry can be charged at an intermediate temperature and heated in stages to observe the effects of temperature change. An example of pressure, temperature, and gas composition data obtained where the autoclave was charged at room temperature and heated to reaction temperature is depicted in Figure 1. One thing to note is that the production of carbon dioxide and the consumption of carbon monoxide is kinetically rapid at temperatures above about 350°C. The experimental conditions for data reported in this paper are given in Table 1.

Coal

The coal utilized in the experiments was a lignite obtained from a mine located near Beulah, North Dakota (Sample B3). Proximate-ultimate data have been presented earlier (2). Lignitic coals are very reactive and are reported to evolve carbon dioxide at temperatures as low as 200°C (3). Dried lignites readily react with air and can spontaneously combust. Coal samples are therefore stored wet under nitrogen in lump form and pulverized just prior to use.

The B3 lignite sample was pyrolyzed in a stream of inert gas at 500°C by Timpe (4) at GFETC under an Associated Western University grant. The sample produced 0.17, 2.05, 14.92, 1.50, and 0.67 wt pct (MAF coal) of H₂, CO, CO₂, CH₄, and C₂-C₄ hydrocarbon gases, respectively. These data are in agreement with previously reported distillation assay data (5). In batch autoclave tests, the total gas discharged at the end of a run is slightly increased over the amount charged due to CO₂ production. For a charge of 3 moles of gas and 50 gm of MAF coal, a CO₂ concentration of about 5 mole pct is typical.

TABLE 1
Experimental Conditions for Reported Studies

Figure-Curve	Run No.	Range of Temp. (°C)	Reactants Charged				Total H ₂ O (gm)
			CO ₂ (moles)	H ₂ (moles)	MAF Lignite (gm)	Solvent (gm)	
2,3	30	400-470	1.8	1.6	44	163	42
2,3	21	400-480	1.8	1.6	--	--	50
2,3	22	400-480	1.8	1.6	--	200	50
4-1	34	400-440	4.0	--	--	--	50
4-2	35	206-440	4.0	--	51	182	1
4-3	32	440	4.0	--	45	164	40
5-4	39-2	400-480	3.1	--	26	92	23
5-5	39-1	350-470	3.5	--	52	192	47
5-6	62	350-470	2.6	--	140	238	63

Lignitic coals also produce about 10 wt pct (MAF coal) of water during pyrolysis. This water was most probably bound as water of hydration (such as in clays or in humic acid structures) and would not be lost during drying at 110°C. This is potentially "inherent" water that could react with carbon monoxide via the shift reaction.

Solvent

The solvent used in the experiments was mainly a commercially obtained anthracene oil. In autoclave work the solvent was spiked with tetralin (about 7 wt pct of the slurry charged) to minimize coking during rapid heat-up. In the observed gas composition changes, the solvent primarily effects methane production (1). As will be discussed later, the solvent does not effect observed CO₂ or CO values and only slightly effects observed H₂ values.

Gas Analysis

Gas samples were analyzed by on-line GC, eliminating any air dilutions. The column used was a 12 to 14-ft, 1/4-inch 316 SS tube packed with Porapak QS. The GC was a Gow Mac maintained at 50°C employing argon as the carrier gas. Utilizing argon carrier gas results in high hydrogen sensitivity (0.02 mole pct), moderate sensitivity for CO₂ and CH₄ (0.1 to 0.3 mole pct), and poor sensitivity for propane (0.5 mole pct). Calibration gas and reactant gases were purchased pre-mixed from a local supplier.

The gas samples were removed from the gas phase of the autoclave. Previous data indicate that CO₂ and CH₄ are preferentially dissolved relative to H₂ and CO (1) in the liquid phase. Ratios of the mole pct of H₂, CO, CO₂, and CH₄ dissolved in the slurry to those in the gas phase were 0.87, 0.74, 1.38, and 1.10, respectively, at 435°C and 4500 psi. However, the value of dissolved gas was 37 ml (STP)/gm slurry; about 0.3 moles for a 200-gm charge, which was an order of magnitude less than in the gas phase, assuming all of the solvent was in the slurry phase. For the solvent in these tests, 40 to 60 pct was in the gas phase; therefore, there would be only about 0.1 to 0.2 moles of dissolved gas, which would have little effect on the composition of the analyzed gas phase. The moles of gas charged plus the moles of methane produced were found to be equal to the moles of gas metered from the autoclave at the end of an experiment plus the gas lost during sampling. Only special experiments enabled the observation of the direct production of CO₂ from lignite. In most cases the moles of CO charged equaled the moles of CO₂ and CO at the end of an experiment.

RESULTS

Experiments have been made to determine how CO and CO-hydrogen interact with the reactor walls, water, solvent, wet coal, and dry coal.

In Runs 21, 22, and 30, H₂-CO (50:50 wt pct) was reacted with water, water-solvent, and water-solvent-coal, respectively, in temperature-stepped experiments. The changes in the gas phase concentrations of CO and H₂ are depicted in Figures 2 and 3. For water and water-oil systems (Fig. 2), CO is slowly consumed only at temperatures above 400°C. Adding wet lignite dramatically increases the consumption of CO even at temperatures below 400°C. In the water-only experiments, the amount of CO consumed is the same as the amount of hydrogen produced. However, in water-oil and in water-oil-coal systems, a slight hydrogen decrease (note expanded scale) is observed (Fig. 3). In systems with oil or oil-coal present, some of the decrease is due to dilution (hydrocarbon gas production and/or the direct production of CO₂ from coal caused an increase of about 10 pct in the total gas in the reactor by the end of a run). As indicated by the data, slightly more H₂ appears to be consumed when coal is present in the oil. These data also illustrate that CO is preferentially reacted at all temperatures.

Figure 4 depicts data for reaction of CO with dry and wet coal-oil slurry. For comparison, data from Run 34 are shown where no coal or oil was present. Run 32 was a hot-charge experiment, which shows the rapid initial CO consumption when wet lignite is present. In Run 35, the lignite was dried in the solvent at 110°C with a nitrogen purge prior to charging. While Run 35 was a slow heat-up with temperature stepping (1 hr at 400°C and 1 hr at 440°C), CO consumption and CO₂ production were essentially complete when 400°C was reached, and very little hydrogen was produced.

The amount of CO consumed has also been found to be dependent on the amount of coal charged. Figure 5 depicts CO consumption when 26, 52, or 140 gms of MAF lignite were charged to the autoclave. For Run 62, where 140 gms were charged, over 95 pct of the CO charged was consumed. The shaded areas (the difference between the top and bottom lines) indicate the moles of H₂ observed versus time. When 140 gms of lignite was present, the amount of hydrogen observed was greatly reduced, indicating that a direct reaction with lignite to produce CO₂ is favored over reactions that would produce both CO₂ and H₂.

CONCLUSIONS

The data that have been presented support the following conclusions:

- a) The shift reaction

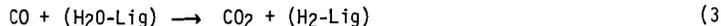


is not catalyzed by the reactor walls or an aromatic solvent (Figs. 2 and 4). However the solvent does undergo some slow hydrogenation (Fig. 3).

- b) The presence of lignite catalyzes the shift reaction, but a reaction such as



or



is favored, especially at lower temperatures (Figs. 1 and 5).

- c) The reported equilibrium values (6) for the shift reaction decrease with increasing temperature from 28.25 at 327°C to 6.3 at 527°C. In runs without lignite, the concentration of CO steadily decreases at all temperatures with time and is at all experimental times far from an equilibrium value. With coal present, the amount of CO consumed is directly dependent on the amount of coal charged. This indicates that the coal has a certain number of reactive sites and that when they have reacted, the reaction essentially stops. While the shift reaction is no doubt occurring, it does not appear to be the most important reaction, at least not in these experiments.
- d) H₂ is produced via the shift reaction (Fig. 5) in CO-H₂O systems. However, since its concentration does not increase when both H₂ and CO-H₂O reactants are present (Fig. 3), hydrogen must be reacting. However, the net consumption of charged hydrogen is small compared to that of CO. Therefore, in competitive reactions CO reacts more rapidly than hydrogen.

The preceding statements re-emphasize the fact that CO undergoes reactions with lignite that are kinetically more favorable than those with hydrogen, and that these reactions are favorable throughout the temperature range studied (350-480°C).

LITERATURE CITED

1. Sondreal, E. A., Knudson, C. L., Schiller, J. E., and May, T. H., "Development of the CO-Steam Process for Liquefaction of Lignite and Western Subbituminous Coals," 1977 Lignite Symposium, GFETC, Grand Forks, N. Dak.
2. Larsen, J. W., "Organic Coal Chemistry," ACS Symposium Series 71, 1978, pp. 301-316.
3. Stach, Braunkohlenarchiv, 40, 1 (1933).
4. Timpe, R., Private communication.
5. Gomez, M, and Goodman, J. B., "Distillation Assays of Missouri River Basin Coals," Report of Investigations 5009, BOM, April 1953.
6. Lavrov, N. V., Korobov, V. V., and Filippova, V. I., "The Thermodynamics of Gasification and Gas-Synthesis Reactions," Macmillan Co., New York, N. Y., 1963.

LIST OF FIGURES

- Figure 1. - Gas phase composition changes with time for a slow heat-up batch autoclave experiment.
- Figure 2. - Temperature and charge composition effects on the CO concentration versus time.
- Figure 3. - Temperature and charge composition effects on the hydrogen concentration versus time.
- Figure 4. - The consumption of CO versus time when 1) $\text{CO} + \text{H}_2\text{O}$; 2) $\text{CO} + \text{dry slurry}$; and 3) $\text{CO} + \text{wet slurry}$ are reacted.
- Figure 5. - The consumption of CO versus time for different amounts of coal. The shaded area (top line minus bottom line) is the moles of H_2 produced.

