Oxidative Degradation of Coals

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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, polyalkylbenzenes, 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 esterfy. 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 coals 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

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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 ($\approx$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 occuring 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 $MgSO_4 \cdot 7H_2O$) 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 $CuSO_4 \cdot 5H_2O$, 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).

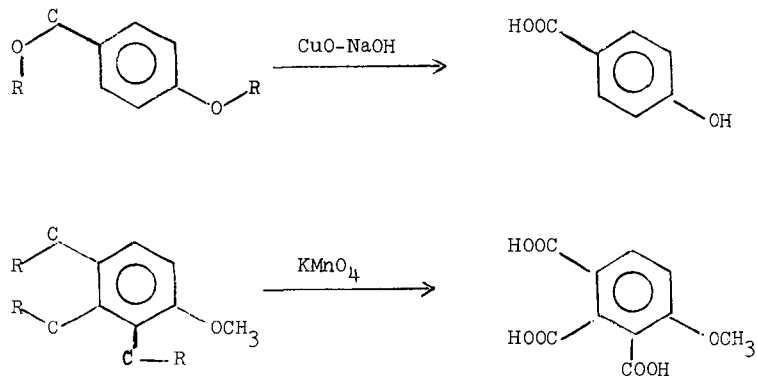
Separation and identification. Insoluble non-volatile samples or products were analyzed by solid probe MS. For each sample, about 50-70 spectra were generally taken between 25°C and 500°C. Oxidation products were esterified and analyzed by GCMS and HRMS. Non-volatile products were examined by LC, solid 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 C_4-C_{21} (with C_9 most abundant) have been identified. Branched dicarboxylic acids (C_5-C_{10}) and tricarboxylic acids (C_6-C_8) 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 C_{14} 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 (HNO_3 or $Na_2Cr_2O_7$) 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 C_{29}; dicarboxylic acid up to C_{20}). 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 C_{18} with max. at C_9) with lesser amounts of phenolic and benzene-carboxylic 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, indenes, 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 tranform 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

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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

Wt %[c)] \ Sample	1	2	3	4	5	6	7	9
Organic acids	52.1	41.3	51.5	19.3	21.2	57.2	52.1	57.8
	(35.3)		(19.6)					(20.3)
Humic Acid-like material	25.1	16.8	45.4			21.6	20.3	
	(55.3)		(62.5)					
Insoluble residue[d)]	14.2	37.6	11.3	26.3	27.1	14.5	30.3	
	(11.0)		(21.0)					(49.3)
Wt% of Identified Acids								
Aliphatic Dicarboxylic Acid $\leq C_7$	11.0	9.5	6.3	2.5	2.2	4.3	2.4	11.8
	(1.8)		(1.0)					(13.2)
Aliphatic Dicarboxylic Acids $\geq C_8$	14.2	9.7	1.1	<0.1	<0.1	<0.1	<0.1	69.3
	(0.8)		(<0.1)					(53.0)
Phenolic acids	11.3	10.4	8.3	87.3	74.8	11.0	1.5	3.4
	(66.6)		(54.1)					(8.6)
Benzenecarboxylic Acids	54.7	55.3	58.9	7.6	13.5	58.4	70.3	5.2
	(26.0)		(36.2)					(9.3)
Oxygen-containing Heterocyclic Acids	6.7	5.8	6.2	<1.0	1.3	7.8	4.9	<0.1
	(<1.0)		(<1.0)					(<1.0)
Others	2.1	9.3	19.2	2.6	8.2	18.5	20.9	10.3
	(3.8)		(7.7)					(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

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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 "ammoxidation" 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 polycarboxyl 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 CO_2; 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 Hypohalite 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 hypohalite 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 CO_2 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 permanaganate 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.

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A Novel Method for Controlled Oxidation*

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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 uM) 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 ($\sim$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

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evolution of CO_2 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 D_2O, pumped dry, and again dissolved in D_2O 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 Me_4Si (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 ^{14}C-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 Krevelen[7] 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 CO_2 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 nonreactive solvent are easily dispersed in Celite by tumbling them together with the solvent and Celite in a rotary evaporator and them removing the solvent under vacuum. This method of dispersal was used in the oxidation procedure described[8] for 4-methyl-2,6-di-tert-butylphenol, a compound found[9] 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] (1) and 2,2',6,6'-tetra-tert-butyl-1,1'-stilbenequinone (2) 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 1, 2, 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 CH_2 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.

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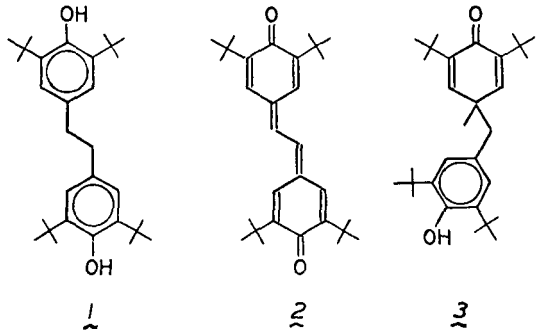

Figure 1. Products of batch oxidation of 4-methyl-2,6-di-tert-butylphenol with potassium permanganate.

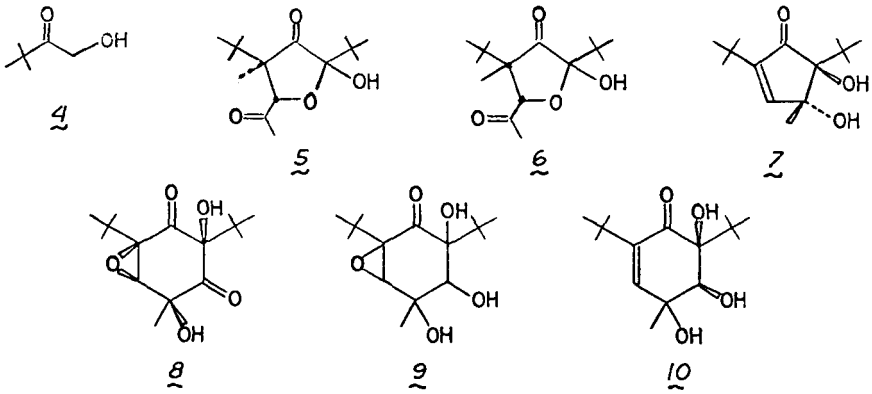

Figure 2. Products of column oxidation of 4-methyl-2,6-di-tert-butylphenol with potassium Permanganate

THE FATE OF SULFUR FUNCTIONS ON OXIDATION WITH PEROXYTRIFLUOROACETIC ACID

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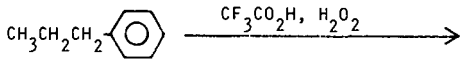
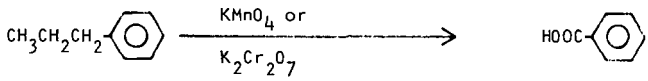
Oxidation has long been one of the primary tools used to probe the chemical structure of coal(1). The newest method is that developed by Deno, who reported that, while the aromatic portions of molecules were rapidly degraded by reaction with hydrogen peroxide in trifluoroacetic acid, the aliphatic skeleton 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



1)



2)

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, $-SO_2R$ and $-SO_3H$, 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

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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 benzenesulfinic acid from phenylethyl phenyl sulfone than from the corresponding sulfones in the other cases. Benzenesulfinic acid would disproportionate (11) or oxidize(12)or both under the reaction conditions to yield benzenesulfonic acid. In fact, phenyl benzenthiolsulfonate, 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.

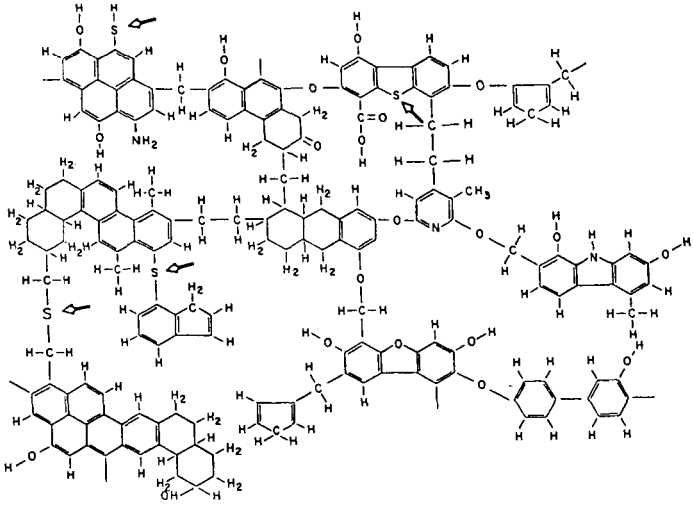

Figure 1. Modified Wiser Coal Structural Model

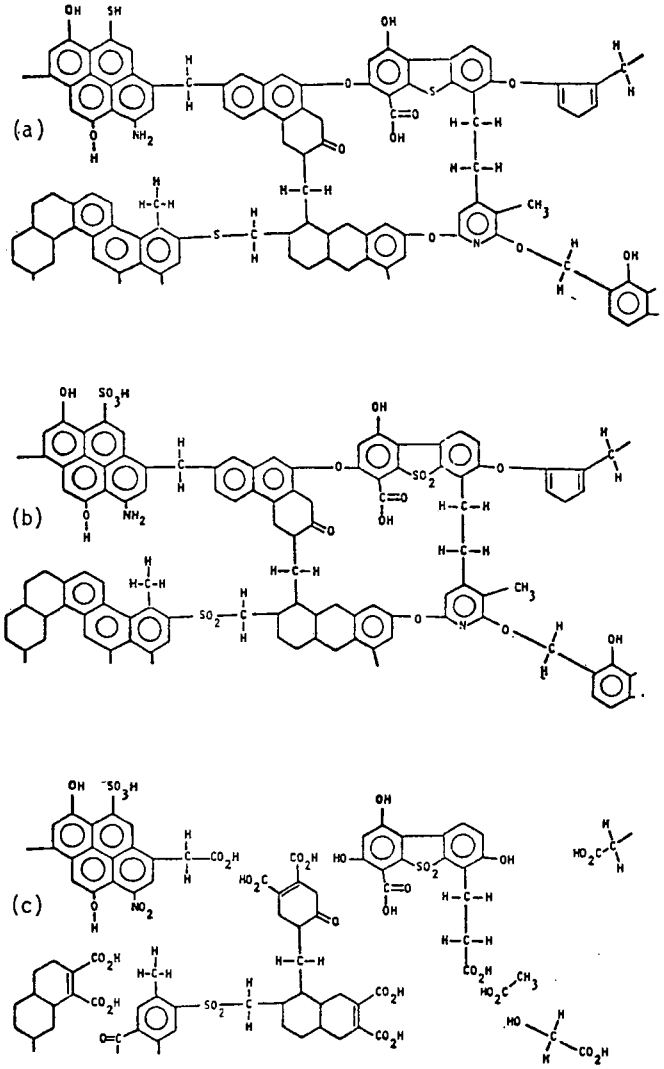

Figure 2. Proposed Effect of Peroxytrifluoroacetic Acid Oxidation on Coal Structure: (a) unmodified, (b) after partial oxidation, and (c) after extensive oxidation.

EXPERIMENTAL

All sulfides were used as obtained from commercial sources, except phenyl 2-phenyl-ethyl sulfide, which was prepared by the reaction of sodium benzenethilate with 2-phenylethyl chloride. Trifluoroacetic acid, 30% hydrogen peroxide and 90% hydrogen peroxide were used as supplied. Infrared spectra were taken on a Beck nn 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 perioxide. 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 smae 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 CF_3CO_3H.

	PRODUCTS (% yield)	
COMPOUND	CF_3CO_3H/H_2O_2, 25°, 15 min	CF_3CO_3H/H_2O_2, 60°, 5 h
Ph-SH	Ph-SO_3H (53%) Ph-S-S-Ph (5%) Ph-S-SO_2-Ph (5%)	Ph-SO_3H (92%)
Ph-S-S-Ph	Ph-S-S-Ph (91%) Ph-SO_3H (5%)	Ph-SO_3H (94%)
$(n\text{-butyl})_2S$	$(n\text{-butyl})_2SO_2$ (99%)	$(n\text{-butyl})_2SO_2$ (99%)
dibenzothiophene	a	dibenzothiophene-5,5-dioxide (91%)
Ph-S-Ph	Ph-SO_2-Ph (95%)	Ph-SO_2-Ph (92%)
Ph-S-CH_2Ph	Ph-SO_2-CH_2Ph (99%)	Ph-SO_2-CH_2Ph (92%)

[a] partially oxidized, sulfide still detectable.

Table 2. OXIDATION OF ω-PHENYLALKYL PHENYL SULFIDES WITH CF_3CO_3H.[a]

$$Ph\text{-}S\text{-}(CH_2)_nPh \longrightarrow PhSO_2(CH_2)_nPh + PhSO_2(CH_2)_nCOOH + PhSO_3H$$

n	sulfone yield	sulfone acid yield	sulfonic acid yield
0	92%	0%	0%
1	91.5%	0.5%	0%
2	55%	8%	16%
3[b]	32%	16%	1%

[a] CF_3CO_2H/H_2O_2 = 1.13/1, 60°, 5 hr, see experimental for work-up procedure.

[b] At 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±12% of the sulfurs.

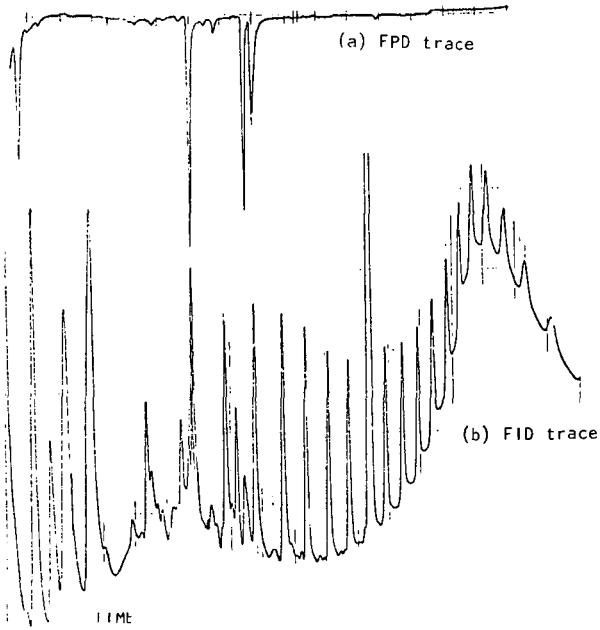

Figure 3. Gas Chromatogram of CH_2N_2-Methylated Product of the Oxidation of Illinois #6 Coal by Peroxytrifluoroacetic Acid.
(a) Flame Photometric Detector; (b) Flame Ionization Detector

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

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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%$\bar{R}_{max}$ (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 Monobasic Acids (as Me esters) (ppm)	Dibasic Acids (as di-Me esters) (ppm)	Ratio Coal/Oxidant (w/w)	Number of Oxidation Steps
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-C_{22} 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 (C_{20}) 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 (C_{20}) n-acids have distributions indicating derivation from fats, particularly the predominance of n-C_{16} and n-C_{18}. 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 C_{20}[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 polyfunctional 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 interpretating 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.

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

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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 ($\bar{M}_n$) 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 $BnNH_2$-extracted coal. However, the finest material would oxidize first and fastest and the coarser residue with $BnNH_2$-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 O_2/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 O_2/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 azo-bis(2-methylpropionitrile) as initiator and t-BuO_2H 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 CO_2. 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 O_2 (2 and 9), $BnNH_2$-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-$NaClO_3$ 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 CO_2, 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 ^{13}C NMR spectra are smaller, but the product of HNO_3 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 CO_2.

MECHANISMS.-- Oxidations in pyridine of both pyridine-extracted coal and the TIPS fraction of the extract with free-radical initiator and added t-BuO_2H (to restrict termination reactions to t-BuO_2• radicals) (2) is slow, incomplete, and inefficient in cleaving coal molecules or fragments. In the conventional free radical-chain mechanism, the $-CH_2-$ and $-CH_2O-$ 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:

$$RH + K\text{-}O\text{-}t\text{-}Bu \rightarrow R^- + t\text{-}BuOH + K^+$$

$$R^- + O_2 \rightarrow R\bullet + O_2\bullet^-$$

The two-step chain cycle is then:

$$R\bullet + O_2 \rightarrow RO_2\bullet$$

$$RO_2\bullet + R^- \rightarrow RO_2^- + R\bullet$$

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:

$$RH + K\text{-}O\text{-}t\text{-}Bu + O_2 \rightarrow RO_2K + t\text{-}BuOH$$

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 CO_2. 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 CO_2.

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 $F_3C\text{-}CO_2H$, H_2O_2, and H_2SO_4 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.

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TABLE 1

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

Experiment No.	21	3[a]	20	22[b]	23	9	11[c]	7[c]	2	6[c]	8	1
Coal fraction	Pyridine extract	Pyridine-extracted			Benzylamine-extracted			Pyridine-extracted		Pyridine extract		Pyridine-extracted
Oxid. agent	← 0.7M NaOCl →					← O_2 →						} 34% HNO_3
Solvent	← H_2O →						DMSO	Pyridine	H_2O	Pyridine	H_2O	
Temperature, °C	← 30 →							← 50 →				60
Initial conc. coal, g/mL	← Decreasing from 0.3 →					← 0.05 →		0.1	0.007	0.1	0.05	~0.02
Steps	3	6	5	2	6	10	4	1	6	1	5	3
Average pH	12.9	10.1	12.9	11.0	13.1	12.9			13.2		12.9	
Reac. time, hr	3.2	2.3	5.3	30	>10	226	12	100	75	32	110	>6.5
Maximum rate[d]	>5	>12	>5	>0.4	> 8	0.8	7	0.14	1	0.1	0.3	>0.05
% of initial C in												
black acids	93.4	43.0	73.3	72.3	65.3	48.8	69.4	6.8[e]	68.0		80.0	64
H_2O-sol.acids	5.8	7.6	7.9	8.3	3.9	3.1	4.9		5.2		3.1	11
undissolved	1.3	7.3	7.3	~0	7.2	24.7	15.3	92	11.1		2.3	1
lost	~0	42.1	11.5	19.4	23.6	23.4	10.4	1	15.7		14.6	24
Analyses of black acids												
% C	59.4	46.3[f]	65.1	54.4	58.8	65.5	62.1		67.8		73.6	55.9
% H	3.66	5.14	3.79	3.30	3.72	4.11	4.07		4.42		4.80	3.04
% N	1.47	1.35	1.61	0.60	1.85	1.58	1.61		1.40		1.60	4.96
% Cl	5.55	6.36	4.69	<0.05	7.08							
% ash	9.2	9	1.43	11.4	8.9						3.5	
%(O+S) by diff.	20.7	>34	22.4	30.3	19.6	28.8	32.2		25.9		16.6	36.1
(H + Cl)/C	0.734	<0.85	0.718	0.723	0.794	0.748	0.772		0.777		0.777	0.659
Oxidizing agent consumed mmole/g coal	15	30	21	11	20	5.63	9.83	3.4	4.44	2.0	3.38	
Analyses of coal fractions used												
% C	74.9	72.5	75.5	65.1[b]	76.0	76.0	76.0	73.8	75.6	79.5	74.9	73.5
% H	4.73	4.44	4.44	3.79	4.76	4.76	4.76	4.52	4.46	5.41	4.73	4.52
% N	1.90	2.10	1.58	1.61	2.36	2.36	2.36	2.19	1.72	2.36	1.90	2.16
H/C	0.752	0.730	0.701	0.718	0.746	0.746	0.746	0.729	0.703	0.82	0.752	0.733

[a] Reference 3. [b] Started with black acids from oxidation 20. [c] Oxidations 6 and 7 in pyridine with 0.06M ABN and 2M or 1M t-BuO_2H, respectively; 11 in DMSO with K-O-t-Bu. [d] In mmoles O_2 (or equivalent)/g coal/ hr. [e] Pyridine-soluble product. [f] M_n = 991; neutral equivalent = 394.

FOURIER TRANSFORM INFRARED STUDIES OF COAL OXIDATION

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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-or-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 intensitives of these bands, so that we can obtain a measure of the number of <u>reactive</u> 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 <u>reduction</u> 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 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, $-COO^-$ 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 $-COO^-$ groups present. If the carboxyl groups are converted to the acid form, -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 $-COO^-$ 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.

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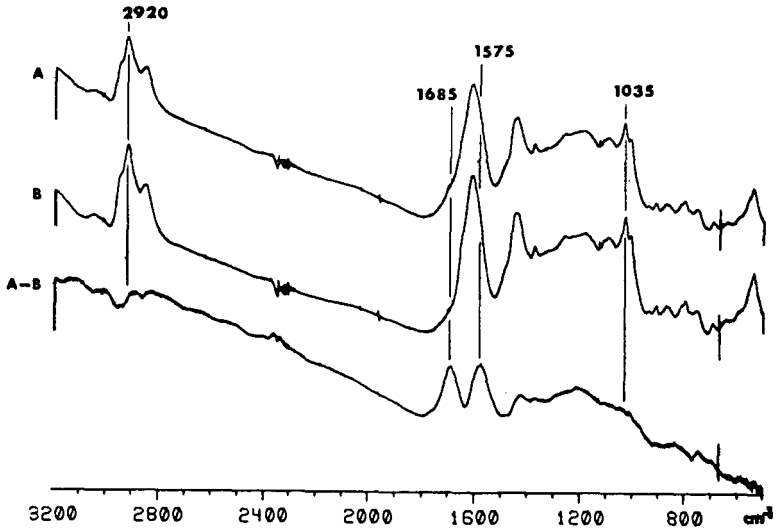

Figure 1: A: FTIR spectrum of coal (PSOC 337) oxidized at 150°C for 2 hours.
B: FTIR spectrum of the original coal (PSOC 337).
A-B: Difference spectrum.

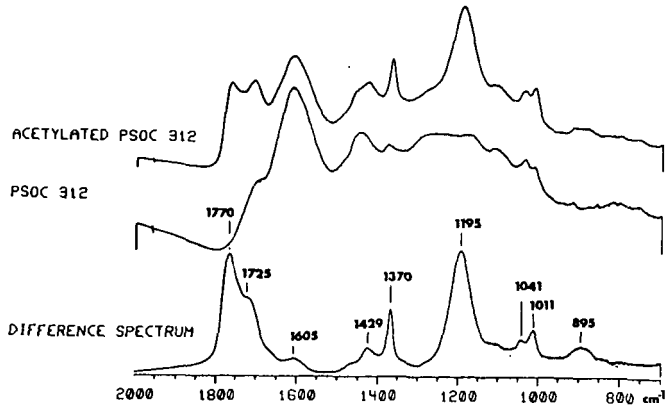

Figure 2: Top: FTIR spectrum of an acetylated Arizona coal (PSOC 312).
Middle: FTIR spectrum of the original coal (PSOC 312).
Bottom: Difference spectrum.

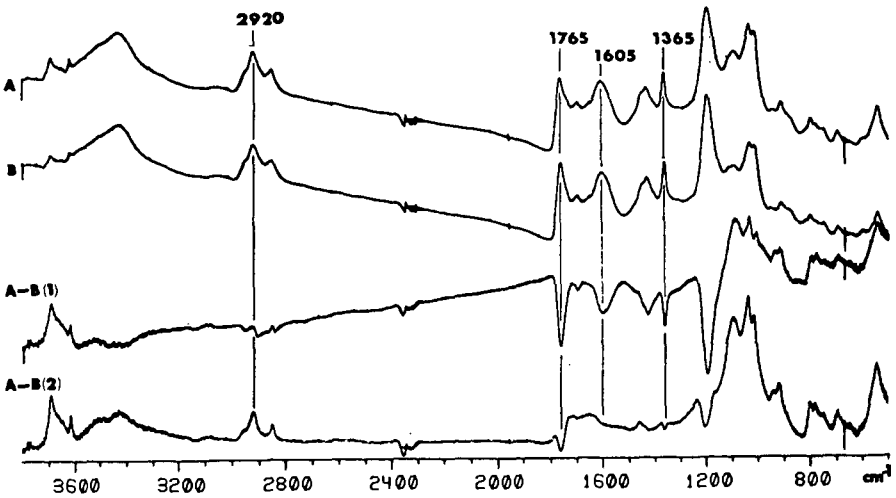

Figure 3: A: FTIR spectrum of acetylated coal (PSOC 337) oxidized at 150°C for 2 hours.
B: FTIR spectrum of acetylated, fresh coal (PSOC 337).
A-B: (1) Difference spectrum subtracting 2920 band to the baseline.
A-B: (2) Difference spectrum subtraction 1605 band to the baseline.

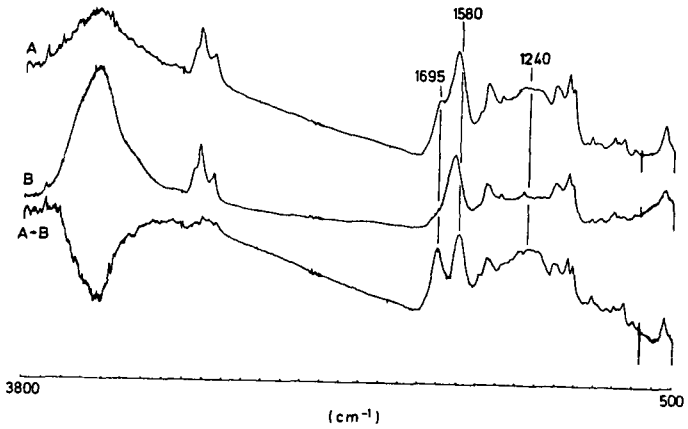

Figure 4: A: FTIR spectrum of oxidized coal after treatment with potassium in THF.
B: FTIR spectrum of oxidized coal.
A-B: Difference spectrum.

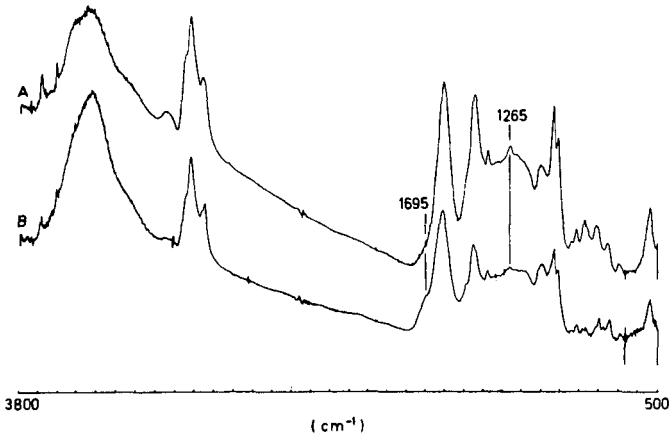

Figure 5: A: FTIR spectrum of fresh, unoxidized coal.
B: FTIR spectrum of unoxidized coal after treatment with potassium in THF.

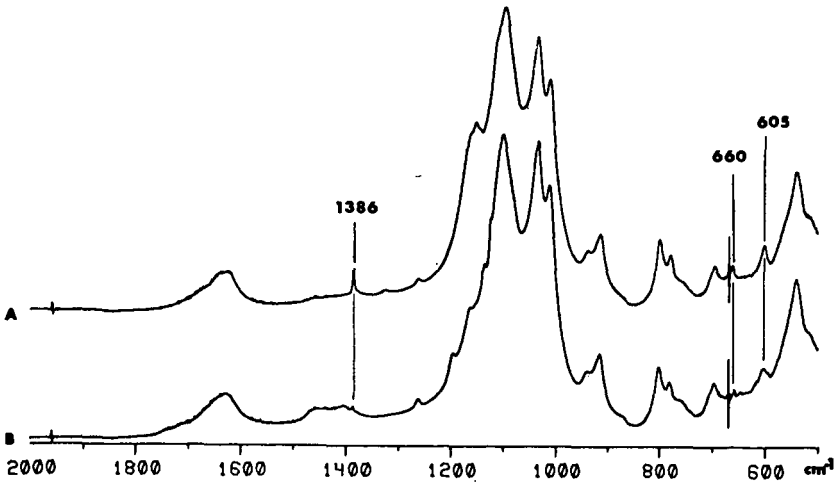

Figure 6: A: FTIR spectrum of low temperature ash (LTA) from highly weathered Canadian coking coal.
B: FTIR spectrum of low temperature ash (LTA) from a less weathered Canadian coking coal.

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

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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 photoautomat MPS 50 automatic 35 mm 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 unusally 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 heterogeniety 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 relevent to the penetration of coal by other gases, vapors, and even liquids.

Acknowledgements

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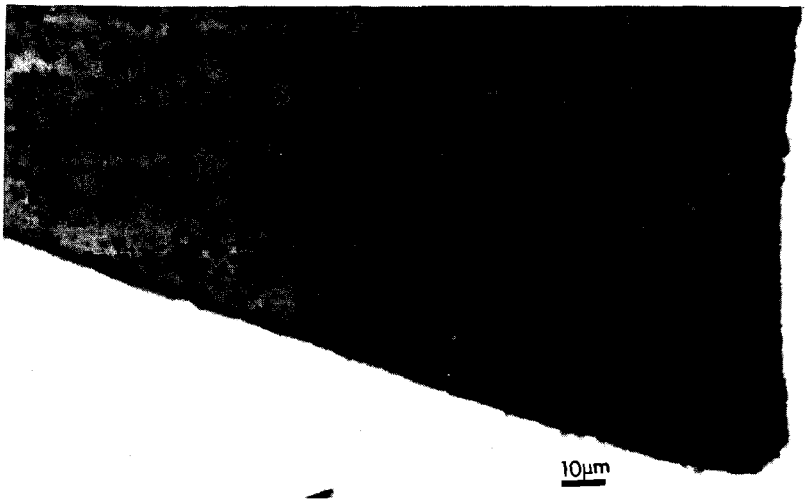

Fig. 1. Thin oxidation border around relatively homogeneous vitrinite

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

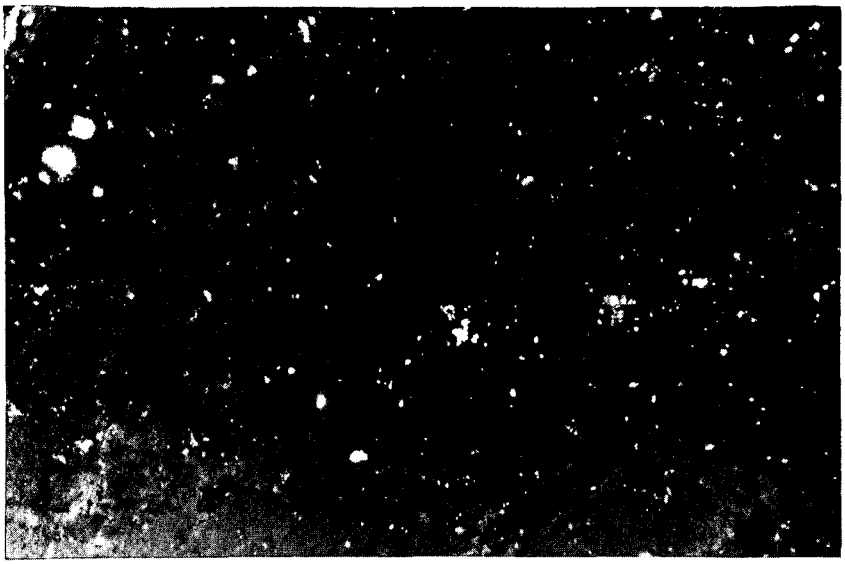

Fig. 3. Reflected light illumination using immersion oil of same area as was shown in Fig. 2

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 ±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 150-200°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 ±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,

$$R_2S \xrightarrow{(O)} R_2SO_x \xrightarrow[\text{base}]{\text{heat and/or}} R\text{-}R + SO_x \qquad 1)$$

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

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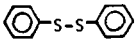
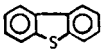
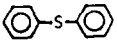
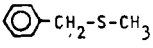
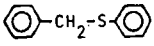
*Operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

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	YIELDS: RECOVERED STARTING MATERIAL	YIELDS: PRODUCTS
	0%	SO_3Na (95%)
	5%	SO_3Na (90%)
	96%	No reaction
	87%	No reaction
	98%	No reaction
$(n\text{-}C_8H_{17})_2S$	90%	No reaction
	36%	CHO (23%), COONa (34%), CH_3SO_3Na (55%)
	29%	CHO (31%), -COONa (18%), SO_3Na (51%)

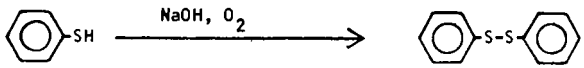
[a] 150°C, 200 psi O_2, 0.2M aqueous Na_2CO_3, 1 hour.

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	Lovilia Coal Added: O_2
Dibenzothiophene	96%	83%	76%
Diphenyl Sulfide	98	76	74
Dioctyl 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



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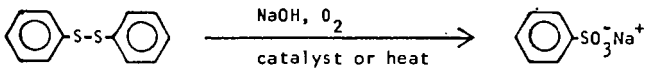


3)

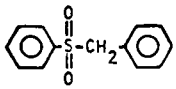
sulfide, to be explained. The fact that it is only the benzylic sulfides which are reactive is reminiscent of hydrocarbon autoxidation, a long known and well studied process which involves the free radical abstraction of hydrogen from weak carbon-hydrogen bonds(9). Table 3 presents the relative rates 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

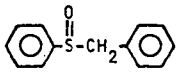
Compound	$Ph^{\cdot}$, 60°C[a]	$(CH_3)_3COO^{\cdot}$, 30°C[b]	RH + ROO·, 30°C[b]
$C_6H_5-CH_3$	(1.0)	(1.0)	(1.0)
$C_6H_5-CH_2CH_2-C_6H_5$	3.6	5.0	2.3
$C_6H_5-CH_2-C_6H_5$	5.1	8.9	8.3
	13.	---	---
$C_6H_5-CH_2S-C_6H_5$	17.	4.4	40.
$C_6H_5-CH_2S-CH_3$	8.2	---	---
$C_6H_5-S-CH_3$	1.4	---	---

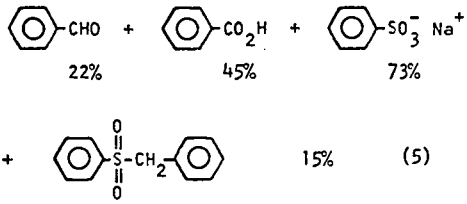
[a]Data of reference 10. [b]Data of reference 11.

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



No Reaction (93% recovery) (4)

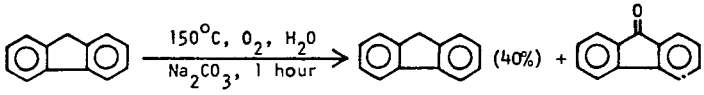




(5)

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.



(6)

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
(P)-CH_2-S-(⬡)	10%
(P)-CH_2-S-(⬡)-CH_3	20%
(P)-CH_2-DBT-CH_2-(P)	0

[a]150°C, 200 psi O_2, 0.2 M aqueous Na_2CO_3, 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]	Ames Processed Extract 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

[a] 150°C, 0.2 M aqueous Na_2CO_3, 1 hour. [b] 200 psi N_2 pressure. [c] 200 psi O_2 pressure.
[d] Samples contain a small amount of ash or NaCl. Element percents are expressed ash or NaCl free.

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14. The details of synthesis will be published in another place.

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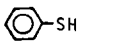
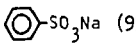
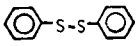
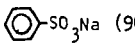
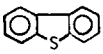
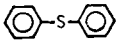
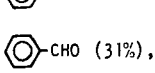
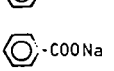
	0%	 (95%)
	5%	 (90%)
	96%	No reaction
	87%	No reaction
	98%	No reaction
$(n\text{-}C_8H_{17})_2S$	90%	No reaction
	36%	 (23%),  (34%), CH_3SO_3Na (55%)
	29%	(31%), (18%), (51%)

[a] 150°C, 200 psi O_2, 0.2M aqueous Na_2CO_3, 1 hour.

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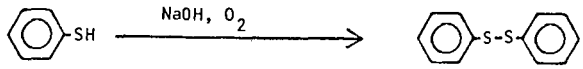

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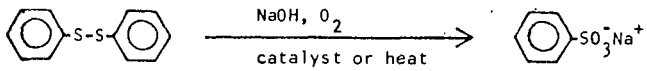

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Compound	$Ph^{\cdot}$, 60°C[a]	$(CH_3)_3COO^{\cdot}$, 30°C[b]	RH + ROO·, 30°C[b]
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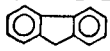
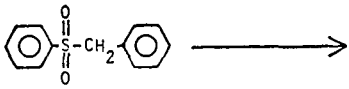
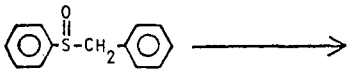
	13.	---	---
$C_6H_5-CH_2S-C_6H_5$	17.	4.4	40.
$C_6H_5-CH_2S-CH_3$	8.2	---	---
$C_6H_5-S-CH_3$	1.4	---	---

[a]Data of reference 10. [b]Data of reference 11.

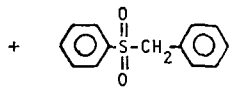
In order to rule out the possibility that the benzylic sulfides are in fact oxidized to either the sulfoxide or sulfone, which then are responsible for the observed products, both benzyl phenyl sulfoxide and benzyl phenyl sulfone were subjected to the reaction conditions. Because the sulfone is inert, 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



No Reaction (93% recovery) (4)



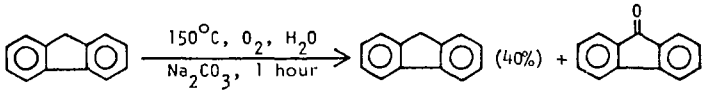
22% 45% 73%



15% (5)

possible reaction intermediate.

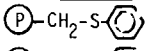
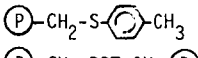
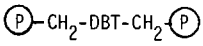
Beside benzylic sulfides, one would expect that some hydrocarbons, for example, fluorene, would also be reactive to the oxydesulfurization conditions. Under Ames process conditions, fluorene is indeed degraded to its known autoxidation product, fluorenone(13). While we have not yet run other hydrocarbons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



(40%) (55%) (6)

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
	10%
	20%
	0

[a]150°C, 200 psi O_2, 0.2 M aqueous Na_2CO_3, 1 hour.

[b]Ⓟ = 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]	Ames Processed Extract 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

[a] 150°C, 0.2 M aqueous Na_2CO_3, 1 hour. [b] 200 psi N_2 pressure. [c] 200 psi O_2 pressure.
[d] Samples 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

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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 10μ 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 cyclohexene-1,2-dicarboxylate
12	34.5	di p-bromophenacyl cyclohexene-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 CF_3CO_3H-H_2SO_4. 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 RuO_4 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

Trifluoroperacetic 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 similarily.

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

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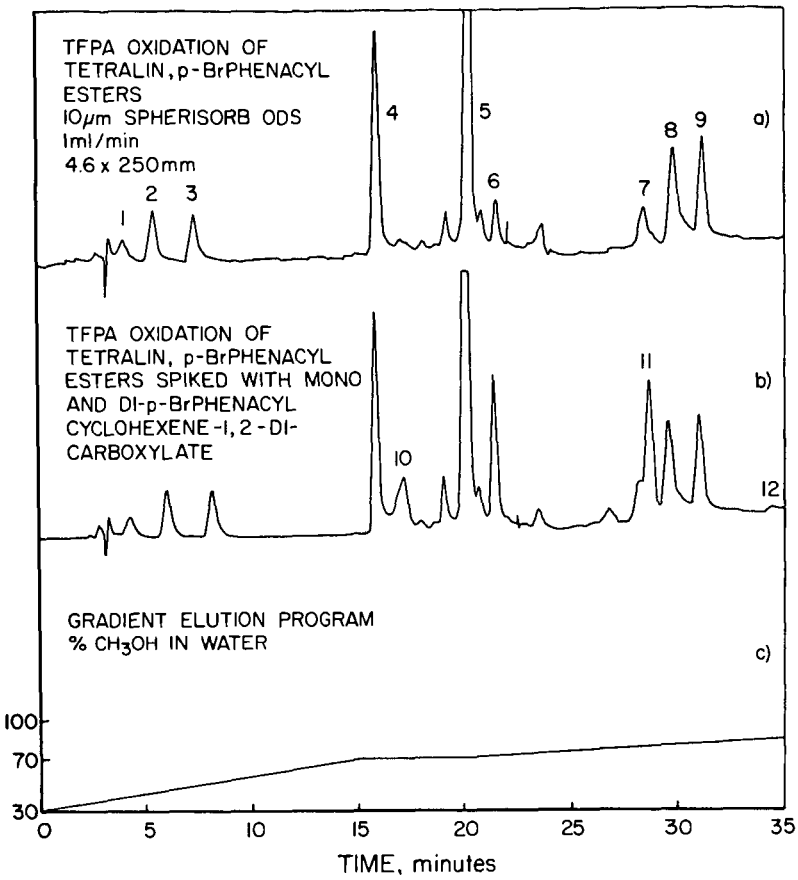

Figure 1. - Separations of p-bromophenacyl esters of tetralin TFPA oxidation products. Peak numbers refer to compounds in Table 1.

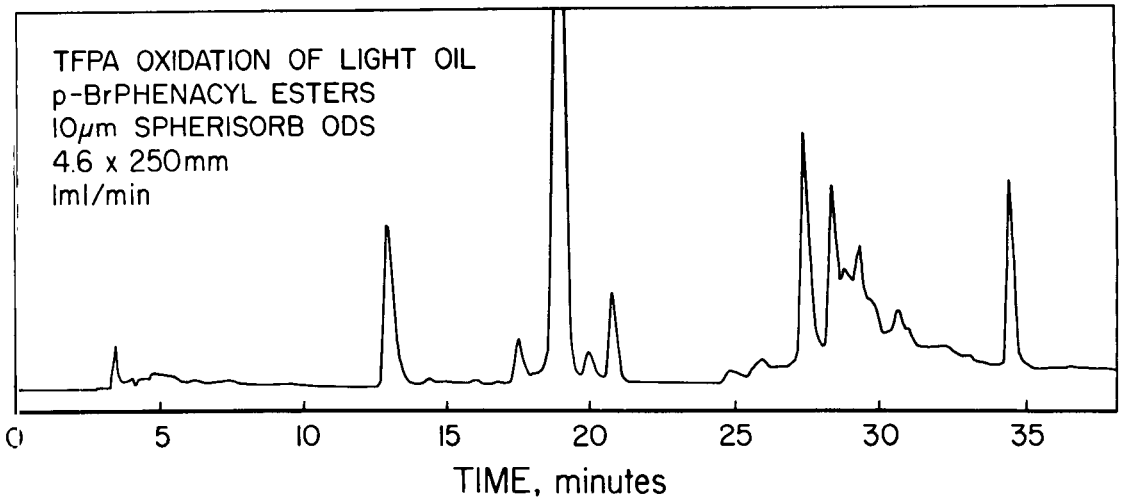

Figure 2. - Separation of p-bromophenacyl esters of light oil TFPA oxidation products.

THE UTILISATION OF HYDROGEN IN UK COAL LIQUEFACTION

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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 kgh^{-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 quantitive 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

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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

Material	Weight without cake washing	Weight with cake washing
Input		
Coal (daf basis)*	100	100
Hydrogen consumed	5.7	6.0
Products		
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_2O, H_2S, 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

Hydrogen In			Hydrogen Out		
Coal (daf basis)	=	5.5	Filter cake	=	0.8
			Hydrocarbon gases	=	2.2
Hydrogen consummed	=	6.0	Heterogases	=	1.1
			Naphtha	=	1.8
			Mid-distillate	=	4.0
			Pitch	=	1.6
TOTAL	=	11.5	TOTAL	=	11.5

$$\text{Hydrogen Retrieval} = \frac{\text{Hydrogen in Liquid Products}}{\text{Hydrogen in Coal + Added Hydrogen}} \times 100 = 66\%$$

Table 4

Products and Hydrogen Consumption after Secondary Refining

Material	Weight without cake washing	Weight with cake washing
Input		
Coal (daf basis)*	100	100
Hydrogen consumed	6.2	6.7
Products		
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.

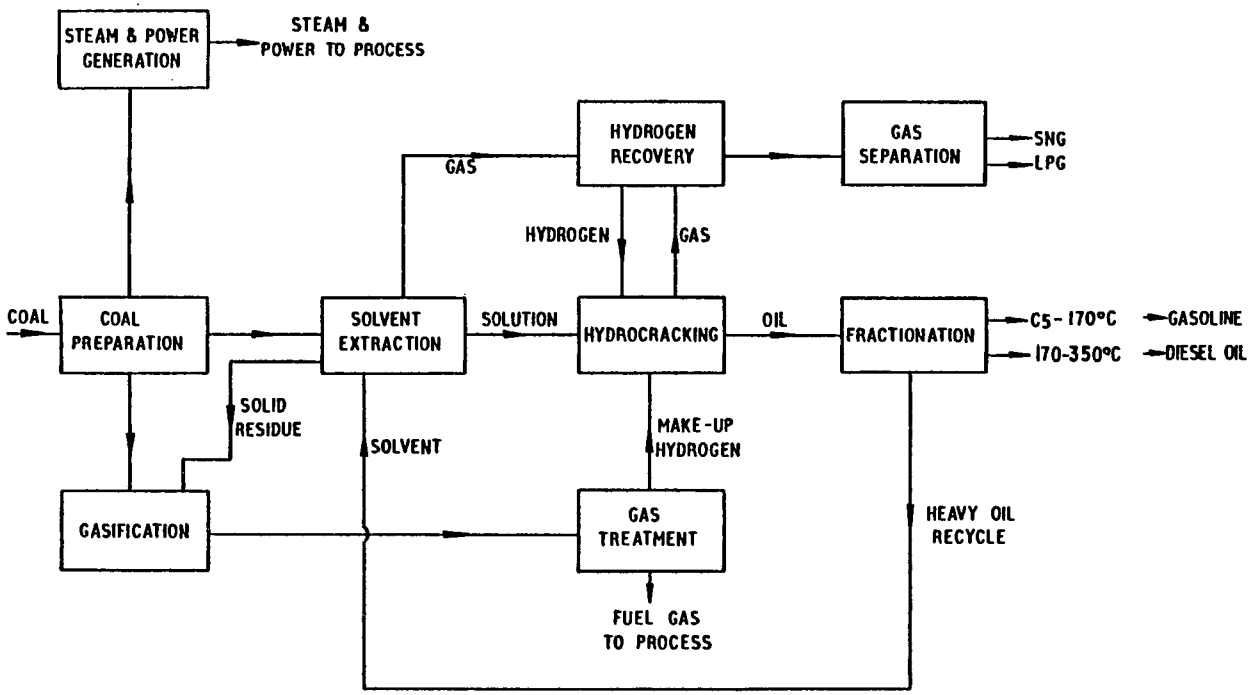

FIG. 1 NCB LIQUID SOLVENT EXTRACTION PROCESS

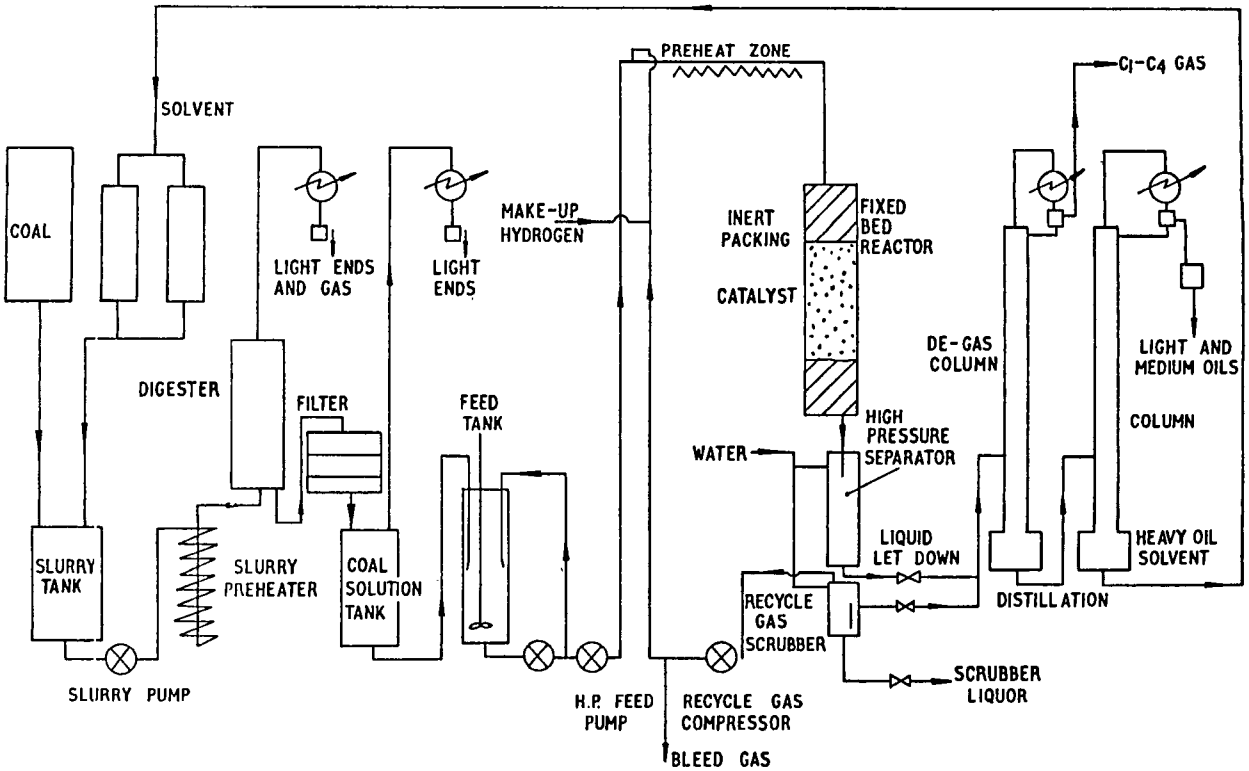

FIGURE 2. INTEGRATED SOLVENT EXTRACTION / CONTINUOUS HYDROCRACKING UNIT

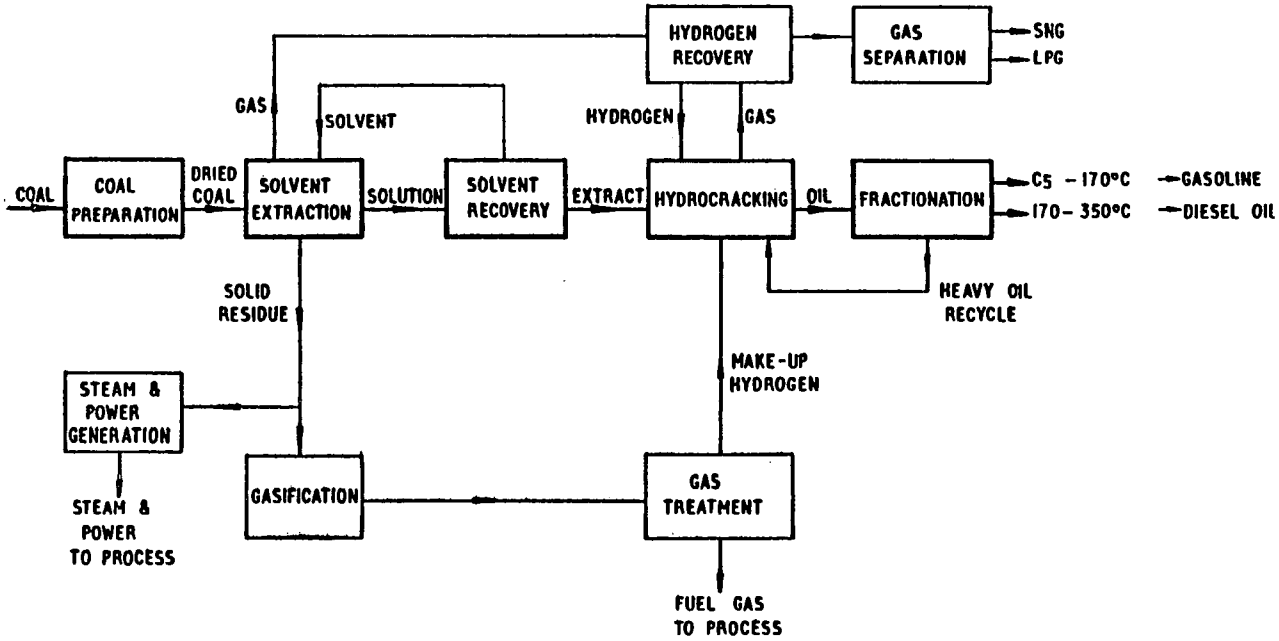

FIG. 3 NCB SUPERCRITICAL GAS EXTRACTION PROCESS