THE EFFECT OF OXIDATION OF COAL ON THE COMPOSITION OF LIQUEFACTION PRODUCTS

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ABSTRACT

In an effort to understand the effect of oxidation of coal on the composition of liquefaction products, a sample of hvAb coal from the Lower Kittanning Seam in Pennsylvania, labelled PSOC-1336, was oxidized in the presence of air in a convection oven at 140°C for 16 days and liquefied in tubing bomb reactors in the presence of tetralin. The oxidation of coal decreased the liquefaction conversion. The aromatic fraction of the hexane-soluble oil from oxidized coal contained smaller amounts of phenanthrenes and pyrenes and larger amounts of tetralin-related artifacts when compared to that from the fresh coal. Relatively larger amounts of the hydroxy derivatives of indane, naphthalene, fluorene and phenanthrene were present in the polar fraction from the oxidized coal.

INTRODUCTION

It is known that coals deteriorate on oxidation and the extent of deterioration depends on the severity of oxidation conditions. The earliest study on the mechanism of oxidation of coals was reported by Jones and Townend in 1945 (1). After a lack of interest for more than two decades, there has been renewed interest in studying the effect of oxidation on the physical and chemical characteristics of coals (2,3). New analytical techniques to detect oxidation (4,5) and the mechanism and kinetics of oxidation have been reported (6,7). Few studies exist on the effects of partial oxidation on the liquefaction behavior of coals (8-10).

EXPERIMENTAL

The objective of this study is to understand the effects of oxidation on the liquefaction behavior of coals and on the composition of liquefaction products. A sample of hvAb coal from the Lower Kittanning seam in Pennsylvania (PSOC-1336) was oxidized by exposure to air in an oven at 140°C for 16 days and then liquefied in tubing bomb reactors using tetralin as donor vehicle under fairly mild conditions (400°C, one hour, no hydrogen gas). The unoxidized coal was also liquefied under identical conditions for comparison.

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RESULTS AND DISCUSSION

The characteristics of the coal are given in Table 1 and the basic liquefaction data are shown in Table 2. The total conversion into ethyl acetate-soluble products plus gases was slightly higher in the case of the unoxidized coal. The higher conversion was reflected in a higher yield of liquid products whereas yield of gases actually decreased. This shows that oxidation is detrimental to coal liquefaction. Similar results have been reported (9,10).

The hexane-soluble oil was vacuum distilled at 70°C (about 2 mm Hg pressure) to remove naphthalene and excess tetralin as completely as possible. A primary fractionation of the oil into saturate, aromatic and polar fractions was made by HPLC (Waters Associates) using a semi-preparative micro-Bondapak NH_2 column. Table 2 does not show appreciable differences with respect to the yield of individual fractions.

All fractions were analyzed by capillary-GC/MS (Finnigan 4000) using a 30 meter SE-54 column to obtain product composition data. The n-alkane distribution in the saturate fraction of the oil from unoxidized coal is compared with that of the oxidized coal in Figure 1. The differences are minor with respect to the modality of distribution as well as the yield of individual hydrocarbons. However, GC/MS characterization of the aromatic fractions revealed important differences.

Figure 2 shows the gas chromatograms of aromatic fractions and the peaks are identified in Table 3. The aromatic fractions contained various dimeric artefacts (hydrogenated binaphthyls) formed from the tetralin donor vehicle during coal liquefaction. Pyrites and clay minerals were found to independently catalyze these reactions (11). Table 4 shows that the yield of selected artifacts, binaphthyl, tetrahydro-, and octahydro-binaphthyl, were much higher when the coal was oxidized.

It is known that exposure of coals to air at temperatures below 80°C, leads to the formation of peroxides (1). These unstable species may be transient intermediates at somewhat higher temperatures, leading to the formation of various oxygen functions, notably carbonyl. Carbonyl is easily reduced if a supply of hydrogen is available, and so will tend to promote both generation of free radicals from the solvent and increased consumption of it. This, perhaps, is the chief factor responsible for the production of dimers from the solvent. Additionally, the oxidation would have converted the pyrite present in the coal (2.1% dmmf) to sulfates and sulfuric acid, which might have influenced the dimerization. In any case, an enhancement in the production of artefacts could limit the availability of hydrogen from the donor solvent which, in turn, can affect the yield of smaller molecules that are formed via hydrocracking and there are obvious implications for recycle solvent quality and consumption.

Benzylic CH_2 groups in diaryl-methanes and diaryl-ethanes are likely to be particularly susceptible for oxidation. Once oxidized, they can no longer cleave to methyl-substituted aromatic structrues. Thus, one might expect methyl substitution to be reduced in the liquefaction products of an oxidized coal. The product yield data in Table 4 for some selected polynuclear aromatic hydrocarbons, lend support to this argument, though they cannot be said to prove it.

The differences in composition of the polar fraction are considerably larger. The oxidized coal afforded a richer, more complex mixture of compounds and structural types than the unoxidized (Figure 3 and Table 5). At the lower end of the molecular weight range, there are large numbers of alkyl-hydroxy-benzenes and alkyl-indanols. The fractions from both oxidized and unoxidized coals showed a number of alkyl-hydroxy-naphthalenes, but in the higher end of the molecular weight range, hydroxy-fluorene and hydroxy-phenanthrenes were more abundant and richer in the polar fractions from the oxidized sample.

A comparison of the FTIR spectra of oxidized and unoxidized coals showed the expected increase due to carbonyl group absorption (1690 cm^{-1}), but also showed an increase of singly-bonded oxygen (ether or phenolic). Reduction of carbonyl and cleavage of ethers, as well as direct insertion of OH, could all contribute to a more complex mixture of phenols in the liquefaction product of an oxidized coal.

CONCLUSIONS

The laboratory low-temperature oxidation of a coking Pennyslvania coal, PSOC-1336, decreases the liquefaction conversion into ethylacetate solubles plus gases. The ratio of dimeric solvent artefacts to coal products was much greater in hexane-soluble oil from the oxidized sample. An enhancement in the yield of solvent artefacts could indirectly affect the yield of smaller molecules that are formed via cracking. The liquefaction products of the oxidized coal contained less methyl substitution but larger amounts of hydroxy derivatives of indane, naphthalene, fluorene and phenanthrene.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Contract No. EX-76-C-01-2494 and the coal used in this study was drawn from the Penn State/DOE Coal Sample and Data Base.

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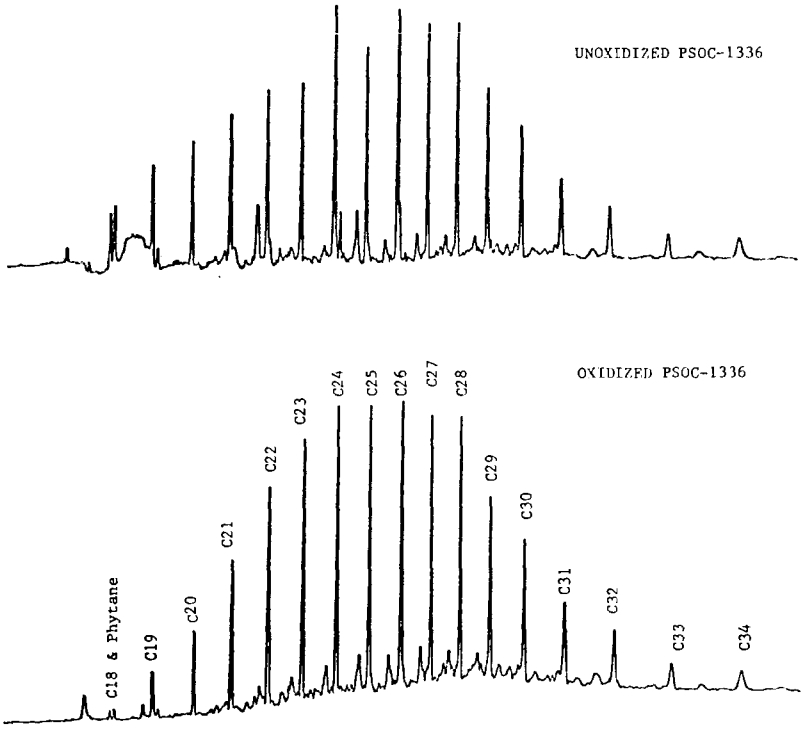

FIGURE 1. TOTAL ION CHROMATOGRAM OF SATURATED FRACTIONS

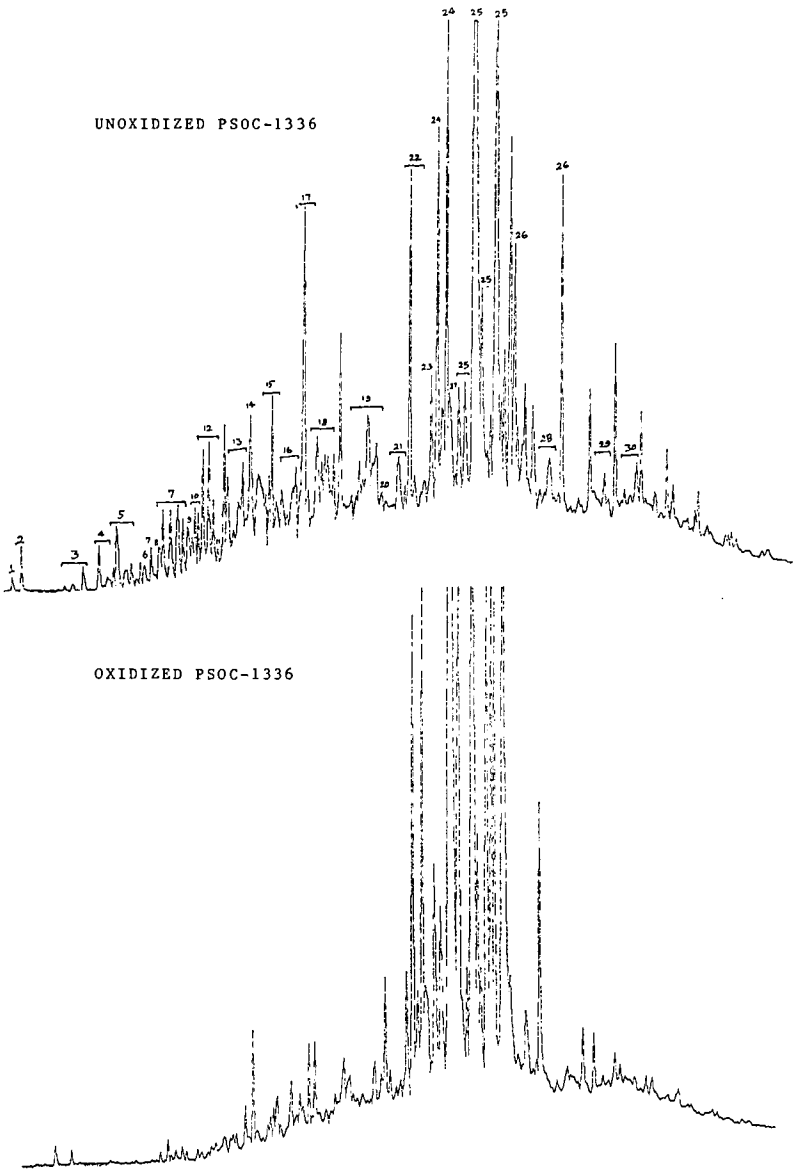

FIGURE 2. TOTAL ION CHROMATOGRAM OF AROMATIC FRACTIONS

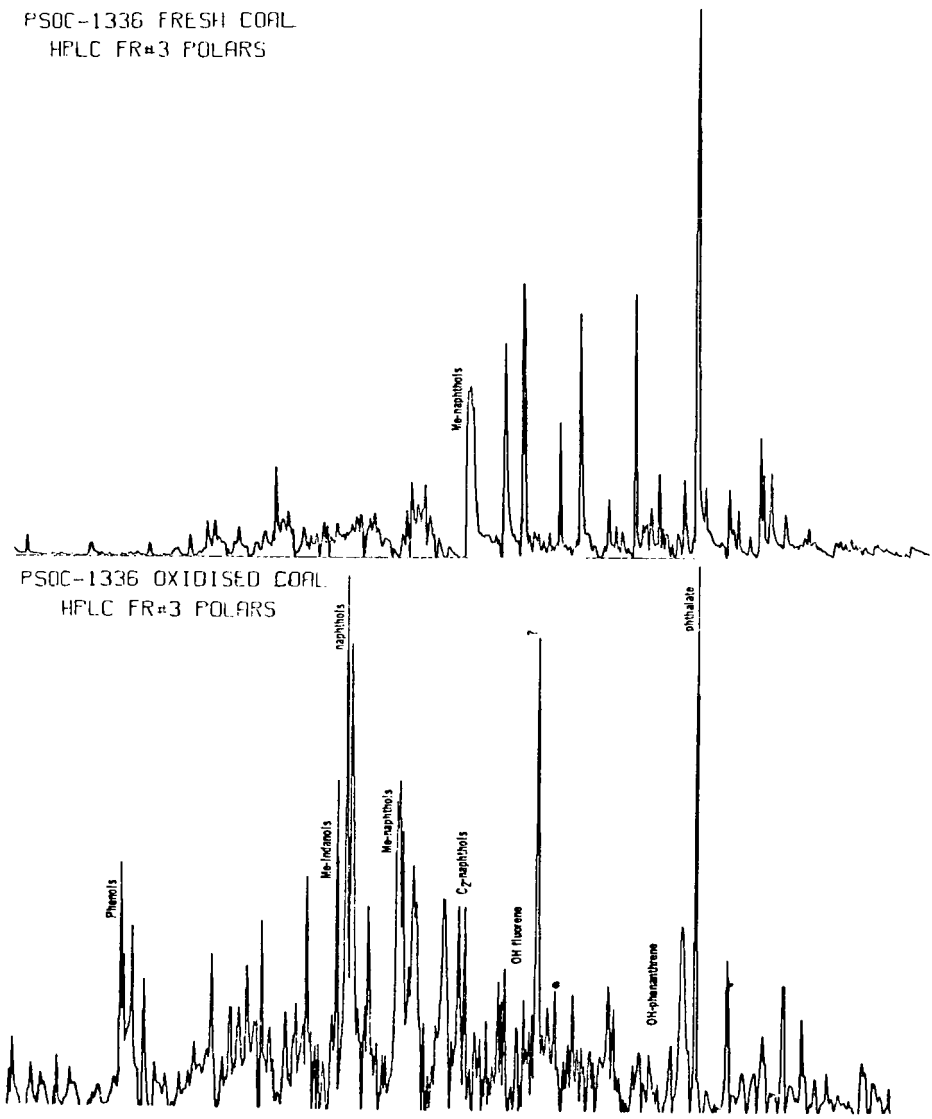

FIGURE 3. TOTAL ION CHROMATOGRAM OF POLAR FRACTIONS

TABLE 1

Analytical Data for PSOC-1336, Lower Kittannning Seam, Pa.

dry mineral matter free			
C	87.2%	vitrinite	85%
H	5.4	liptinites	5%
N	1.6	inertinite	10%
S	1.0	dry basis:	
Cl	0.1	mineral matter	16.7% (including pyrite 2.1%)
O(diff)	4.6		

ASTM rank class: hvAb

TABLE 2

Liquefaction Data

	Unoxidized	Oxidized
Product Yields:(%dmmf coal)		
Asphaltenes	19.9	14.9
Oil	11.0	7.2
Gases	3.3	7.2
Conversion	34.2	29.3
Oil Composition:(% oil)		
Saturates	2.8	2.6
Aromatics	42.3	40.0
Polars	54.9	57.4

TABLE 3

Identification of Aromatic Hydrocarbons

Peak Number	Identification
1	Tetralin
2	Naphthalene
3	Methylnaphthalene
4	Tetrahydromethylnaphthalene
5	C_2-Naphthalene
6	Acenaphthene
7	C_3-Naphthalene
8	C_1-Acenaphthene
9	Fluorene
10	C_1-Biphenyl
11	C_2-Acenaphthene
12	C_1-Dibenzofuran + C_4-Naphthalene
13	C_2-Dibenzofuran/C_2-Biphenyl
14	Phenanthrene
15	C_3-Biphenyl
16	C_4-Biphenyl
17	C_1-Phenanthrene
18	C_2-Phenanthrene
19	Fluoranthene/C_3-Phenanthrene
20	Pyrene
21	C_3-Phenantherene
22	C_1-Pyrene
23	Benzofluorene
24	Tetrahydrobinaphthyl
25	Octahydrobinaphthyl
26	Binaphthyl
27	Chrysene/Triphenylene/ Benzanthracene, Methyl
28	Benzofluoranthene
29	Benzopyrene/Perylene
30	Benzopyrene/Perylene, Methyl

TABLE 4

Yields of Selected Components in the Aromatic Fraction of PSOC-1336

	Unoxidized	Oxidized
Artefacts (ug/gm oil)		
Binaphthyl	73	290
Tetrahydrobinaphthyl	103	336
Octahydrobinaphthyl	211	348
Total artefacts	387	973
Coal-derived (in ug/gm dry coal)		
Phenanthrene	3.3	1.8
C_1-Phenanthrenes	11.3	5.6
C_2-Phenanthrenes	18.1	8.8
Pyrene	3.0	2.5
C_1-Pyrenes	23.7	16.5
C_2-Pyrenes	25.3	20.4
C_3-Pyrenes	8.1	5.0
Benzopyrene and its isomers	28.5	26.8

TABLE 5

Compounds identified in the Polar Fraction *

Phenol	Naphthol
Methylphenol	Methylnaphthol
C_2-Phenol	C_5-Phenol
C_3-Phenol	C_2-Naphthol
Indole	Hydroxyfluorene
Indanol	C_1-Dibenzofuran
Dihydroxybenzene	Xanthene
C_4-Phenol	C_1-Hydroxyfluorene
Indenol	C_2-Hydroxyfluorene
Methylindanol	Hydroxyphenanthrene
Methylindole	Diisobutylphthalate (impurity)
C_2-Indanols	
Phenylfuran	

* From Oxidized Coal