

Chemical Changes In Coal Liquefaction

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Mobil Research and Development Corp. supplied five coals and their soluble and insoluble fractions after 3 mins solvent refining and their soluble fraction after 90 mins solvent refining. All samples were oxidatively degraded with $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{SO}_4$. The major effects of solvent refining on molecular structure were the large increases in arylmethyl, arylphenyl, and total aromatic material.

Liquefaction (solvent refining) of coal involves thermolysis of benzyl-oxygen and/or benzyl-benzyl bonds as the first step in the depolymerization. This view derives from NMR studies¹, studies with model compounds^{1,2}, and oxidative degradations with $\text{Na}_2\text{Cr}_2\text{O}_7$ ³ and $\text{CF}_3\text{CO}_2\text{H}$ ⁴. The oxidative degradations with $\text{CF}_3\text{CO}_2\text{H}$ are now extended to five new coals. Products have been determined from the original coal, the soluble and insoluble fraction after 3 mins. and the soluble fraction after 90 mins. The data are summarized in Tables 1 and 2.

The best method for determining the amount of arylmethyl groups in coals is from the yield of acetic acid formed in oxidative degradation with $\text{CF}_3\text{CO}_2\text{H}-\text{H}_2\text{SO}_4$ ⁴⁻⁶. The data from this method are shown in Table 1. The following observations and interpretations are made.

1. A sharp increase in arylmethyl accompanies liquefaction in all five coals and in two coals which were studied earlier⁴. This increase is the result of thermal cleavage to benzyl radicals and abstraction of hydrogen atoms by the benzyl radicals to form arylmethyl.

2. All five coals give about the same percentage increase in arylmethyl after 90 mins of solvent refining, but not after 3 mins. This indicates that benzyl radicals form from more than one type of structure. Arylmethyl formation is 87-99% complete in the last three coals in Table 1 after 3 mins whereas it is only 33% and 50% complete in the first two coals. Based on studies of model compounds^{1,2}, it is attractive to ascribe arylmethyl formation in 3 mins to cleavage of benzyl ethers and slower cleavage to bibenzyl structures. Despite the obvious oversimplification, this is the best estimate as yet of the relative amounts of C-O and C-C cleavage. It is also direct evidence for bibenzyl structures in PSOC 372 and 330 and the first direct evidence for such structures in any coal.

3. It might have been expected that the more arylmethyl, the more cleavage, and the more SRC. In fact the opposite is shown in Table 1. The conflict would be resolved if coal liquefaction depended more on certain critical cleavages and the conversion of a 3-dimensional polymer to a 1-dimensional polymer than on the total amount of cleavage and the extent of depolymerization.

4. The amount of arylmethyl in the residue (3 min) is about the same as in the original coal. This indicates that arylmethylys do not play any role in liquefaction as expected.

5. No higher homologs of acetic acid were observed indicating the absence of arylalkyls above methyl.

The data in Table 2 show that biaryl structures are rare or absent in the original coals but appear in significant quantity on liquefaction. The foremost evidence for this are the changes in yields of benzoic acid (column 136). This product was not observed from any of the five coals, but it was an important product from SRC (solvent refined coal). Model studies have shown that benzoic acid forms from biphenyl and other biaryls in which one of the phenyl rings is unsubstituted. It does not form from alkylbenzenes, a variety of polyaromatics, and many other model compounds^{5,6}.

There are three other products in Table 2 whose appearance or increase indicate biaryl structures. These are benzene-1,4-dicarboxylic acid (194b), benzene-1,3-dicarboxylic acid (194c), and benzene-1,3,5-tricarboxylic acid (310b). All have non-adjacent carboxyl groups. These are more characteristic of biaryl structures in contrast to fused aromatics which form products with adjacent (1,2) carboxyls.

We interpret the appearance of simple phenyl substituents to the reductive removal of the heteroatom in benzothiophenes, benzofurans, and possibly benzopyrroles. If one of the benz rings is unsubstituted, such a reductive hydrogenolysis would create a simple phenyl group attached to the remaining polymer by a biphenyl type of bond. While phenyl groups would also be generated by hydrogenolysis of fluorenes, fluorenes are expected to be stable under the conditions of liquefaction.

On the basis of oxidative degradations of Illinois no. 6 and Wyodak coals before and after liquefaction, it was concluded that the aromatic structure increases on liquefaction⁴. The evidence was an increase in phthalic (benzene-1,2-dicarboxylic) acid, which is the dominant product from most polyaromatic systems⁵.

The increase in aromatic structure is also shown by certain lactones which are minor products from oxidation of a variety of polyaromatic hydrocarbons⁵. They appear from oxidation of the solvent refined samples but not from the original coals (Table 4).

Oxidation of coals with 40% HNO₃ at 60° provides a reliable method for determining the amounts and lengths of linear alkane chains in coals by converting such chains to linear diacids of two less carbons⁷. As expected, the amounts and lengths showed no change on solvent refining on Illinois no. 6 Monterey coal.

Illinois no. 6 Monterey coal and Wyodak coal showed marked decreases in the yields of succinic acid after solvent refining⁴. This was interpreted as showing a marked decrease in dihydrophenanthrene structures. This decrease in succinic acid product is not shown by the five coals in Table 2. It is possible that dihydroaromatic structures donate hydrogen to benzyl radicals but are regenerated by transfer of hydrogen from solvent to the coal polymer.

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EXPERIMENTAL

The samples were kindly provided by Dr. D. D. Whitehurst of Mobile Research and Development Corporation. The parent coals were bituminous and had been originally obtained from the Penn State Coal Base and carry their code number.

The procedure for oxidation with $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$ is identical to that reported earlier⁵. The analysis and conversion to methyl esters was modified as follows.

The acetic acid was determined from the proton magnetic resonance spectrum of the filtered reaction mixture. The area of the acetic acid peak was compared to the area of the peak of a weighed amount of DSS as originally described⁵. This method is preferable to the distillation method⁵ providing line broadening is not too severe.

The isolation of the methyl esters has been made more quantitative by modifying the procedure for isolation. The removal of volatile material and the conversion to methyl esters was unchanged⁵. After esterification with BF_3 in methanol, 100 cm³ of saturated aqueous NaCl was added and the mixture³ extracted with three 35 cm³ portions of CH_2Cl_2 . The combined CH_2Cl_2 extracts were washed with 100 cm³ of 3% NaHCO_3 followed by washing with saturated aq. NaCl. A weighed amount of acetophenone was added as an internal standard. The solution was dried over MgSO_4 . The responses to the detector in the gas chromatogram were calculated from effective carbon numbers as before⁵.

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Table 1 Yields of acetic acid from oxidative degradations with $\text{CF}_3\text{CO}_3\text{H}-\text{H}_2\text{SO}_4$

Name	Penn State coal base number ^a				
	372 Kentucky Imboden	330 Penn. Middle Kittaning	256 Penn. Lower Freeport	312 Arizona Red	405 Oklahoma Lower Hartshorne
% liquified ^a (3 min)	79	70	65	51	25
% C (maf)	85.9	83.5	88.2 ¹	78.4	89.8
rank	HVA	HVB	med. vol.	HVC	low vol.
	Yield of acetic acid (meq. per g of maf) ^b				
parent coal	0.44	0.33	0.31	0.42	0.31
SRC (3 min)	0.77	0.74	1.05	1.46	1.51
SRC (90 min)	1.45	1.15	1.06	1.60	1.69
residue (3 min)	0.33	0.41	0.27	0.27	0.24

^aSamples and liquefaction data were supplied by D. D. Whitehurst, Mobil Research and Development Corp.

^bThe percentages of moisture (m) and ash (a) are available from the Penn State Coal Base computer printouts. The SRC samples had negligible moisture or ash. In calculating the yields of acetic acid from the residue, it was assumed that all of the ash in the coal was retained in the residue in correcting to a maf (moisture and ash free) basis.

Table 2 Absolute yields (mg per g maf) of products^a from oxidative degradations with CF₃CO₃H-H₂SO₄

MW of methyl ester	132	146	136	204	218a	218b	194a	194b	194c	276	252a	252b	310a	310b
PSOC-372														
coal	17.7	4.9	---	1.2	0.7	4.3	---	---	---	1.3	3.3	---	2.1	---
SRC (3 m)	10.5	3.7	2.3	0.5	0.7	5.6	---	0.9	0.7	2.0	2.0	0.8	0.9	0.1
SRC (90 m)	13.7	6.8	3.5	0.6	0.5	7.2	---	2.4	1.3	2.0	6.7	2.4	2.4	0.4
res (3 m)	7.6	0.7	0.6	0.3	0.7	1.6	1.0	0.4	0.4	0.2	2.8	---	1.7	0.3
PSOC-330														
coal	21.0	6.1	---	1.2	0.9	2.3	---	0.2	0.2	1.5	1.5	---	1.6	---
SRC (3 m)	18.4	6.8	6.1	1.0	0.4	10.0	---	2.4	---	2.6	6.0	---	1.7	0.2
SRC (90 m)	2.5	7.1	7.1	0.1	0.7	2.8	7.7	4.9	3.2	3.0	9.3	0.1	4.4	1.0
res (3 m)	5.1	4.2	1.5	0.1	0.3	0.6	0.5	0.4	0.4	0.6	2.2	---	1.9	0.7
PSOC-256														
coal	18.7	3.9	---	1.1	0.6	1.6	0.2	0.5	0.4	0.9	3.2	---	2.2	---
SRC (3 m)	6.8	6.2	5.9	0.1	0.8	0.7	2.0	1.9	1.9	2.7	9.3	0.2	5.3	0.7
SRC (90 m)	5.8	8.4	6.6	0.4	1.0	10.2	3.2	3.3	2.3	3.5	12.0	0.1	0.5	1.1
res (3 m)	12.5	3.1	2.3	1.0	0.2	2.4	1.7	0.8	0.6	1.6	7.1	---	2.9	0.5
PSOC-312														
coal	13.8	4.9	---	2.0	1.8	10.7	---	---	0.5	2.8	2.5	0.2	1.1	0.2
SRC (3 m)	6.7	12.8	5.9	1.6	0.8	10.4	---	3.3	---	2.8	3.9	1.3	0.9	0.2
SRC (90 m)	11.7	14.3	4.8	0.3	1.8	6.7	---	2.6	3.1	3.3	8.2	0.1	2.8	0.4
res (3 m)	14.8	3.4	1.6	1.2	0.6	4.9	0.7	0.5	0.7	1.6	3.3	0.2	2.3	0.5
PSOC-405														
coal	7.9	2.4	---	0.6	0.1	2.5	1.3	0.9	0.5	0.8	2.5	0.2	1.0	0.3
SRC (3 m)	3.5	10.7	5.8	0.2	1.4	5.2	2.8	3.6	2.7	2.6	7.2	0.2	4.5	0.6
SRC (90 m)	0.9	9.1	5.3	0.3	1.8	1.3	4.0	6.9	---	3.6	9.1	0.2	2.9	0.4
res (3 m)	10.9	3.9	2.4	0.2	0.5	2.8	2.5	1.6	1.8	3.6	10.0	---	6.1	1.1

^aIdentified in Table 3.

Table 3 Identification of products in Table 2

MW of methyl ester	Relative GC ret. time	Name of corresponding acid (X is COOH)
132	3.20	malonic acid (XCH_2X)
146	4.60	succinic acid (XCH_2CH_2X)
136	5.15	benzoic acid
204	9.23	1,1,2-ethanetricarboxylic acid
218a	10.54	1,2,3-propanetricarboxylic acid
218b	10.97	oxiranetricarboxylic acid
194a	11.10	benzene-1,2-dicarboxylic acid
194b	11.33	benzene-1,4-dicarboxylic acid
194c	11.58	benzene-1,3-dicarboxylic acid
276	14.33	oxiranetetracarboxylic acid
252a	15.79	benzene-1,2,4-tricarboxylic acid
252b	16.14	benzene-1,3,5-tricarboxylic acid
310a	19.18	benzene-1,2,4,5-tetracarboxylic acid
310b	19.50	benzene-1,2,3,5-tetracarboxylic acid

Table 4 Absolute yields (mg per g maf) of selected minor products from oxidative degradations with $\text{CF}_3\text{CO}_3\text{H-H}_2\text{SO}_4$

	MW of products containing N										MW of lactones					
	209	239	253	297	311	192	250b	250c	250d	250e	264	308a	308b	322		
PSOC-372																
coal	---	---	0.4	0.4	0.4	---	---	---	---	0.1	---	0.4	0.3	---		
SRC (3 m)	0.2	---	---	0.4	---	0.2	---	0.2	0.2	---	---	0.3	tr	---		
SRC (90 m)	0.3	---	---	---	---	0.8	0.5	0.5	0.7	0.1	---	0.6	0.3	---		
res (3 m)	0.1	0.5	---	0.4	---	---	---	0.1	---	---	---	---	---	---		
PSOC-330																
coal	---	0.1	0.2	0.4	0.5	---	---	---	---	---	---	0.3	0.4	---		
SRC (3 m)	---	---	---	---	---	0.2	0.2	0.2	0.2	---	---	0.5	0.3	---		
SRC (90 m)	0.3	0.3	---	0.7	---	0.2	0.5	0.5	0.3	0.7	0.3	0.7	1.0	0.4		
res (3 m)	---	0.2	---	---	---	---	---	---	0.2	0.5	---	---	0.7	---		
PSOC-256																
coal	---	0.1	0.3	0.6	0.2	---	---	---	---	0.2	---	0.1	0.3	---		
SRC (3 m)	---	0.4	---	1.1	---	---	0.7	0.3	0.1	0.6	---	0.2	0.7	---		
SRC (90 m)	0.2	---	---	---	---	0.3	0.5	0.4	0.5	0.3	---	1.3	1.0	---		
res (3 m)	---	0.2	---	0.3	---	---	---	---	---	---	---	0.3	---	---		
PSOC-312																
coal	---	---	---	0.3	---	---	---	---	---	0.1	---	0.4	0.4	---		
SRC (3 m)	---	---	---	---	---	0.4	0.5	0.8	0.3	0.2	---	0.3	---	---		
SRC (90 m)	0.3	---	---	---	---	0.3	0.4	0.2	0.4	0.2	0.2	0.6	0.4	0.2		
res (3 m)	0.2	0.1	---	0.7	---	---	---	0.1	---	---	---	---	0.4	---		
PSOC-405																
coal	---	---	---	0.1	---	---	tr	tr	---	tr	---	0.1	tr	---		
SRC (3 m)	---	0.6	---	1.8	---	0.2	0.4	0.2	---	0.6	0.2	0.4	0.2	0.2		
SRC (90 m)	0.6	0.5	---	3.4	---	0.8	0.9	0.2	0.3	1.1	---	0.2	0.2	0.4		
res (3 m)	0.4	0.9	---	3.1	---	---	---	0.9	---	---	---	---	0.4	---		

Table 4 (continued)

^aThe following identifications (somewhat speculative) are based on MW from chemical ionization mass spectra, the number of carbonyls from the MW of the CD₃OH ester, and fragmentation in electron impact mass spectra. The MW's in the Table are of the methyl esters and the following names are of the corresponding carboxylic acids: 209, 3-carboxypyridine-2-acetic acid; 239, pyridine-2,x,y-tricarboxylic acid (the 2-COOH does not esterify); 253, pyridine-3,4,5-tricarboxylic acid; 297, pyridine-2,3,4,5-tetracarboxylic acid (the 2-COOH does not esterify); 311, a pyridinetetracarboxylic acid.

The lactones (named as the corresponding hydroxy acid) were as follows: 192, 2'-carboxyphenyl-2-hydroxyacetic acid (a major product from naphthalene); 250b-e, analogs of 192 with an additional carboxyl on the benzene ring (one at each of the four positions); 264, 2'-carboxyphenyl-3-hydroxypropanoic acid; 308a and b, analogs of 192 with two carboxyl groups on the benzene ring; 322, the analog of 264 with an additional carboxyl group on the benzene ring.