SEPARATION AND CHARACTERIZATION OF COAL LIQUIDS FROM WILSONVILLE

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ABSTRACT

Ion-exchange and silica gel adsorption techniques were used to isolate and characterize six distillate cuts from three coal liquids generated at the Advanced Coal Liquefaction Facility in Wilsonville, Alabama. Distillates from Black Thunder subbituminous coal liquids contain much higher levels of acidic components than the distillates of Illinois No. 6 or Pittsburgh No. 8 bituminous coal liquids. Saturate fractions of 450-650 °F distillates of all coal liquids were mainly straight chain aliphatics with some indication of branching. The major components identified in the acid fractions from the Black Thunder coal liquid were methyl, ethyl, propyl, and vinyl substituted phenols, benzaldehydes, and methoxy-benzenes. The major components identified in the base fractions from these liquids were methyl and ethyl substituted quinolines, benzene substituted quinolines and carbazoles, methyl-acridines, methyl substituted phenanthrolines and anthracenecarbonitriles. The major aromatic components of the aromatic fractions from Black Thunder coal liquid were methyl, ethyl, and vinyl substituted benzenes and naphthalenes, methyl-anthracene, methyl and ethyl substituted phenanthrene, fluoranthene, pyrene and chrysene.

INTRODUCTION

A typical coal liquid mixture contains a wide range of compound types including acidic, basic, neutral, and various hydrocarbons. The objective of this investigation was to fractionate distillates from coal liquids of varying rank, characterize the fractions and identify the major components of the fractions. Six distillate cuts of three coal liquids from the Advanced Coal Liquefaction Facility in Wilsonville, Alabama, were selected. The samples were 450-650 °F and 650+ °F distillates of coal liquids from Black Thunder subbituminous and Illinois and Pittsburgh seam bituminous coals. The yields of these fractions as a percentage of MAF feed coal are given in Table I.

EXPERIMENTAL

Samples were separated into acid, base, and neutral (ABN) fractions using a non-aqueous ion-exchange separation technique in which a sample dissolved in cyclohexane is passed through two consecutive ion-exchange LC columns. The first was packed with anion resin and the second with cation resin. The material which is not retained by either column was the neutral fraction. Acids were extracted using formic acid in toluene and bases using propylamine in toluene. The fractions were then filtered and stripped of solvent. The neutral fractions were separated into saturate and aromatic (Sat/Ar) fractions using an activated silica gel column. The saturates were eluted from the column with cyclohexane. The retained aromatics were eluted using a mixture of methanol, diethylether, and toluene.

Proton (^1H) NMR spectrometry was used to study the molecular structure of saturate and aromatic fractions. FT-IR spectroscopy was used to study the functional groups in the acid, base, saturate and aromatic fractions from distillates of Black Thunder coal liquid. Thermogravimetric analysis (TGA) in combination with FT-IR was used to determine the decomposition of neutral fractions from 450-650 °F cuts. A gas chromatograph/mass spectrometer (GC/MS) unit was used for detailed characterization and component type identification of acid, base, neutral, saturate and aromatic fractions from distillates of Black Thunder coal liquid.

RESULTS AND DISCUSSION

Separation Data - Recoveries from acid, base, and neutral (ABN) separation cuts are shown in Table II. The ABN recoveries of the 650+ °F cuts of the Illinois and Pittsburgh coal liquids were reasonable and were within the expected ranges. However, that of the neutral fraction from the lower boiling distillate (450-650 °F) was low, possibly due to the loss of light components of the neutral fraction.

Recoveries from the separation of the neutral fractions into saturate and aromatic fractions are shown in Table II. While the saturates and aromatics of the lower boiling distillates (450-650 °F) were clear and thin brownish liquids, respectively, the saturate and aromatic fractions from the higher boiling distillates (650+ °F) were opaque solids and thick brownish liquids. The total recoveries for higher boiling distillates were reasonable, but the total recoveries for the lower boiling distillates were low. Significant amounts of light components were lost from the aromatic fractions of 450-650 °F cuts.

Elemental Analyses Data - Elemental analyses and calculated H/C ratio are given in Table III. The atomic H/C ratio is highest for the saturate fractions, intermediate for the acid, base, and neutral fractions and lowest for the aromatic fractions. The acid fractions have the highest oxygen and the base fractions have the highest nitrogen content. Neither fraction is free of other heteroatoms. In general, the lower boiling cuts had higher oxygen contents than the higher boiling cuts.

NMR Spectrometry Data - The proton NMR data of the saturate and aromatic fractions of both cuts from Black Thunder coal liquid are shown in Table IV. The saturate fractions of 450-650 °F cuts were mainly straight chain aliphatics with some branching. The aromatic, olefinic, and alpha proton values shown for the saturate fractions of light distillates are negligible. While the aromatic fraction of the 450-650 °F distillate exhibits aromatic compounds with highly branched aliphatics attached to the ring(s), the aromatic fraction of the 650+ °F distillate exhibits aromatics with mostly linear aliphatics. Some methyl substituted aromatics were also present in this fraction.

FTIR Spectroscopy Data - FTIR spectra were obtained for the acid, base, saturate and aromatic fractions of both distillates from Black Thunder coal liquid. Spectra of the acid and base fractions of the 650+ °F cut are shown in Figure 1. The main difference between the FTIR spectra of the acids and bases is the presence of a broad band in the 3600-3100 cm^{-1} region of the spectra of the acids. The broad band in this region is assigned to the absorption of O-H and/or N-H groups associated with the intermolecular hydrogen bonding in phenolic, hydroxyl and pyrolytic type compounds. The aromatic C-H stretches are evident from the peaks in the 3050-3000 cm^{-1} and 900-680 cm^{-1} regions of the acid fractions. The peak assigned to the aromatic C=C stretch at 1600 cm^{-1} is also present in the spectra of the acid fraction. Alkanes, both $-CH_2-$ and $-CH_3$ groups, are also evident in the 2960-2850 cm^{-1} region of the spectra of the acids. Carbonyl bands (1710-1700 cm^{-1}) can be assigned to the carboxilic acid functional group (COOH). Comparison of spectra of the acid fractions of the 450-650 °F and 650+ °F cuts suggests that; 1. the intensities for the bands assigned to the aromatic ring substitutions (900-680 cm^{-1}) are much lower for the acid fraction from 450-650 °F cut, 2. the aromatic to alkane ratio is higher for the acid fraction of high boiling cut, and 3. the methyl functionalities are slightly higher in the acid fraction from 650+ °F distillate.

The aromatics were still evident in the FTIR spectra of the base fractions, but at a much lower concentration. The presence of the carbonyl peak at 1727 cm^{-1} and the pattern of the bands in the aromatic ring substitution region (900-680 cm^{-1}) suggest the presence of 1,2-disubstituted ester compounds. Alkanes ($-CH_2-$ and $-CH_3$) were also evident. The spectra patterns for the two base fractions were nearly identical. The only differences between the spectra of the two bases from the two cuts were the higher ester to alkane and aromatic ratios for the 650+ °F cut.

TGA-FTIR Analyses Data - Stack plots of selected bands from TGA-FTIR analyses of 450-650 °F Black Thunder neutrals are shown in Figure 2. At a TGA temperature up to 300 °F, the neutrals from the Illinois and Pittsburgh coals show very little loss of functional groups. However, the neutral from the Black Thunder coal liquid indicates significant losses of $-CH_2-$ and $-CH_3$ functional groups at about 150 °F. There are significant losses of aliphatic, aromatic, phenolic and C-H stretch functional groups from all three neutrals at temperatures above 300 °F.

GC/MS Analyses Data - GC/MS chromatograms were obtained for the acid, base, neutral, saturate and aromatic fractions of both distillates from Black Thunder coal liquid. Only selected major components were identified. While there are some similar components in both acid fractions from the high and low boiling cuts (i.e. methyl, ethyl, and propyl-phenols), substituted pyrene and fluoranthene are only present in the acid fraction from the 650+ °F cuts. The major components identified in both acid fractions were methyl, ethyl, propyl, and vinyl substituted phenols, benzaldehydes, and methoxy-benzenes. Methyl substituted carbazoles were also seen in both acid fractions.

The major components identified in the base fraction of 450-650 °F cut were methyl and ethyl substituted quinolines. 2,4-Dimethyl-benzaldehyde, which was identified in both acid fractions, was also identified in the two base fractions. 3-propyl-phenol and anthracene were seen in both the acid and base fractions of 450-650 °F distillates, and components such as pyrene and fluoranthene were seen in the acid and base fractions of 650+ °F distillate. The base fraction of the 450-650 °F cut contained benzene substituted quinolines and methyl substituted acridines, and the base fraction of the 650+ °F cut were methyl substituted phenanthrolines, anthracenecarbonitriles, and benzene substituted carbazoles.

The saturates of both distillate cuts were mostly straight chain alkane with limited branching. Some components with functional groups such as hydroxylamine and alcohols were also identified. The major components of the aromatic fraction of the 450-650 °F cut were methyl, ethyl, and vinyl substituted benzenes and naphthalenes. Those in the aromatic fractions of the 650+ °F cut were methyl and ethyl substituted phenanthrene, fluoranthene, pyrene and chrysene.

CONCLUSIONS

The first step in the analysis of coal-derived liquids is the separation of coal liquid into fractions. Distillates from Black Thunder subbituminous coal contain much higher levels of acidic components than those derived from the bituminous coals. The saturate fractions of all coal liquids were mainly straight chain aliphatics with some branching. The aromatic fraction of the low boiling cut derived from Black Thunder coal liquid contained highly branched aliphatics attached to the rings. However, that of the high boiling cut contained both branched and linear aliphatics attached to the rings. The acid fractions of the distillates derived from Black Thunder coal liquid were methyl, ethyl, propyl, and vinyl substituted phenols, benzaldehydes, methoxy-benzenes, methyl substituted carbazoles, and substituted anthracenes, pyrenes and fluoranthenes. The base fractions of the distillates derived from Black Thunder coal liquid were methyl and ethyl substituted quinolines, benzene substituted quinolines, methyl substituted acridines, methyl substituted phenanthrolines, anthracenecarbonitriles, and benzene substituted carbazoles. The aromatic fractions of these distillates contained methyl, ethyl, and vinyl substituted benzenes, naphthalenes, and anthracene, phenanthrene, fluoranthene, pyrene and chrysene.

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Table I

Yield of Distillate Cuts (Wt.%, MAF Feed Coal)) from Coal-Derived Liquids of Illinois No. 6, Pittsburgh No. 8 and Black Thunder

Feed Coal	Fraction	Yield
Black Thunder	450-650 °F	60
	650+°F	2
Illinois No. 6	450-650 °F	40
	650+°F	31
Pittsburgh No. 8	450-650 °F	44
	650+°F	20

Table II

Recoveries (Wt.%) from Acid, Base, Neutral, Saturate and Aromatic Separations of Distillate Cuts from Illinois No. 6, Pittsburgh No. 8 and Black Thunder

Coal Liquid Cut	Acid	Base	Neutral	Total Recovery
B.T. (450-650 °F)	13.30	3.27	70.10	87.30
Ill. No. 6 (450-650 °F)	3.24	4.18	73.60	81.10
Pitt. No. 8 (450-650 °F)	4.66	3.06	90.60	98.30
B.T. (650+ °F)	17.80	5.42	75.40	98.60
Ill. No. 6 (650+ °F)	3.51	2.95	86.20	92.60
Pitt. No. 8 (650+ °F)	7.32	3.74	90.40	101.50

	Saturate	Aromatic	Total Recovery
B.T. (450-650 °F)	25.2	63.3	88.5
Ill. No. 6 (450-650 °F)	23.8	38.6	62.4
Pitt. No. 8 (450-650 °F)	26.8	45.3	72.1
B.T. (650+ °F)	19.8	81.7	101.5
Ill. No. 6 (650+ °F)	23.4	75.1	98.5
Pitt. No. 8 (650+ °F)	26.2	73.4	99.6

Table III

Elemental Analyses (Wt.%) of Acid, Base, Neutral, Saturate and Aromatic Fractions of Distillates from Illinois No. 6, Pittsburgh No. 8 and Black Thunder

Fractions	C	H	N	O	S	H/C
BT (450-650 °F)						
Acid	77.84	8.34	1.71	8.08	0.13	1.28
Base	81.66	8.99	4.43	2.73	0.18	1.31
Neutral	86.55	10.08	< 0.30	-------	0.12	1.39
Saturate	84.39	13.13	< 0.30	-------	870 (ppm)	1.85
Aromatic	88.31	9.25	< 0.30	-------	639 (ppm)	1.25
Ill.#6 (450-650 °F)						
Acid	78.41	8.60	1.57	9.47	0.47	1.31
Base	80.16	9.30	3.80	3.64	0.18	1.38
Neutral	87.99	11.55	< 0.30	------	427 (ppm)	1.56
Saturate	86.12	12.93	< 0.30	------	------	1.79
Aromatic	89.09	9.73	< 0.30	------	568 (ppm)	1.30
Pitt.#8 (450-650 °F)						
Acid	77.78	8.61	0.72	10.15	0.32	1.32
Base	78.50	9.60	2.04	8.89	0.38	1.46
Neutral	88.45	11.63	< 0.3	-------	371 (ppm)	1.57
Saturate	85.47	11.13	< 0.3	-------	------	1.55
Aromatic	88.69	9.85	< 0.3	-------	385 (ppm)	1.32
BT (650+ °F)						
Acid	81.47	7.67	1.25	7.74	772 (ppm)	1.12
Base	84.62	8.20	4.10	1.79	0.36	1.15
Neutral	89.52	9.52	< 0.3	------	399 (ppm)	1.27
Saturate	83.97	14.01	< 0.3	------	239 (ppm)	1.99
Aromatic	89.60	8.04	< 0.3	------	291 (ppm)	1.07
Ill.#6 (650+ °F)						
Acid	82.06	8.44	2.11	5.82	0.29	1.23
Base	83.83	8.89	3.55	2.09	------	1.26
Neutral	89.12	9.97	< 0.30	------	315 (ppm)	1.33
Saturate	86.12	11.83	< 0.30	------	------	1.64
Aromatic	90.27	8.88	< 0.30	------	393 (ppm)	1.17
Pitt.#8 (650+ °F)						
Acid	80.46	8.06	1.00	8.63	0.24	1.19
Base	81.80	8.87	1.70	7.13	0.58	1.29
Neutral	89.50	10.27	< 0.3	------	219 (ppm)	1.37
Saturate	86.25	11.70	< 0.3	------	------	1.62
Aromatic	90.28	9.14	< 0.3	------	289 (ppm)	1.21

Table IV

Proton NMR Data (atom%) from Saturate and Aromatic Fractions of Distillates from Illinois No. 6, Pittsburgh No. 8 and Black Thunder

Sample	Aromatic	Olefinic	Alpha	Methylene	Methyl
BT (450-650 °F)					
Saturate	0.7	0.8	1.4	69.8	27.4
Aromatic	20.5	0.9	32.9	36.8	8.9
Ill.#6 (450-650 °F)					
Saturate	0.4	0.2	0.6	68.5	30.4
Aromatic	17.2	1.0	33.2	39.3	9.3
Pitt.#8 (450-650 °F)					
Saturate	0.2	0.3	0.9	67.8	30.7
Aromatic	15.6	0.8	32.1	41.4	10.1
BT (650+ °F)					
Saturate	0.3	0.4	0.8	78.0	20.5
Aromatic	29.3	1.2	30.2	32.5	6.9
Ill.#6 (650+ °F)					
Saturate	0.8	0.6	1.7	71.2	25.8
Aromatic	21.5	0.8	30.3	37.9	9.5
Pitt.#8 (650+ °F)					
Saturate	0.3	0.4	1.3	71.7	26.3
Aromatic	20.1	0.8	29.8	39.0	10.3

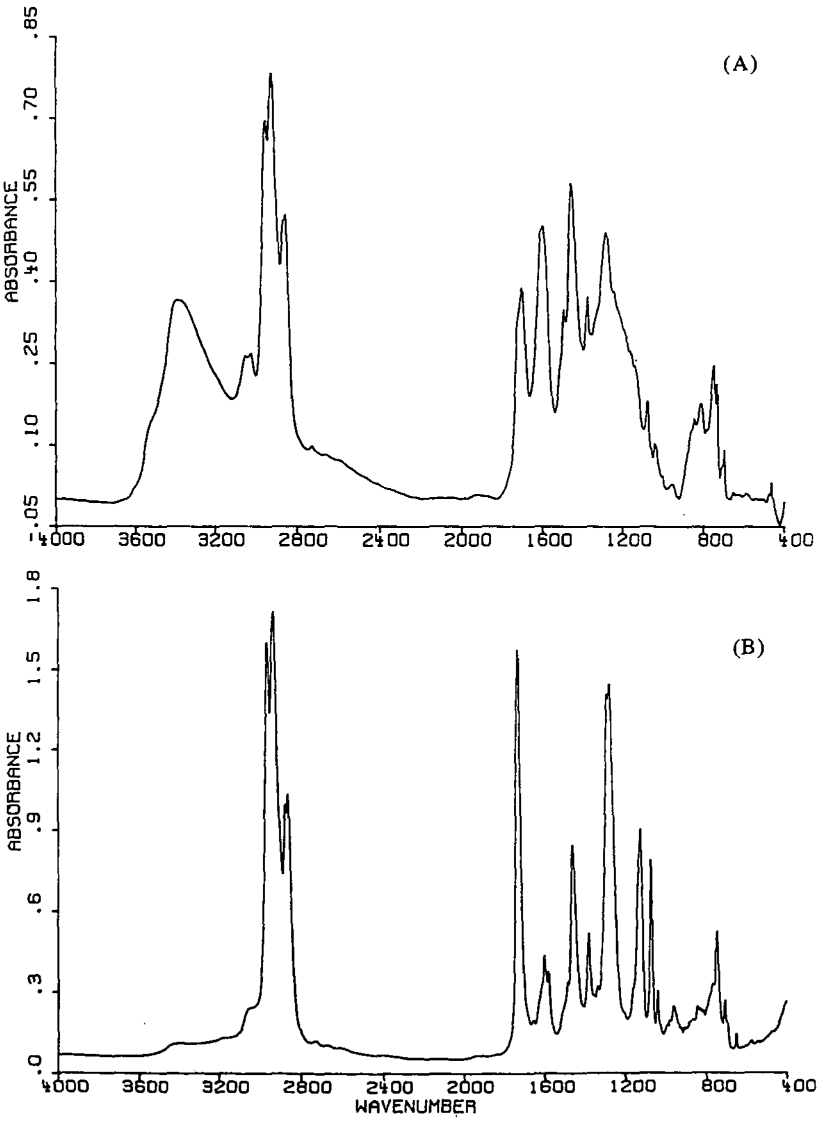

Figure 1. FTIR Spectra of Acid (A) and Base (B) Fractions from 650+ °F Distillate cut of Black Thunder Coal Liquid.

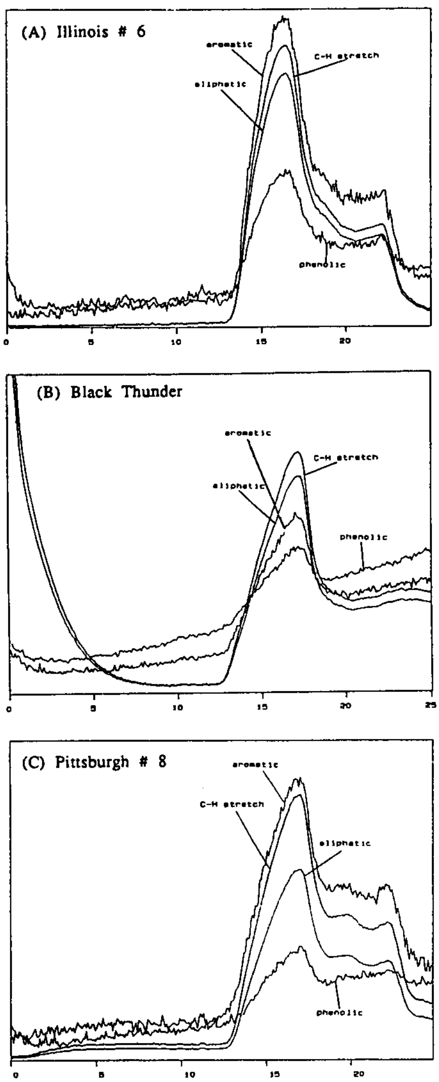

Figure 2. Stack Plots of Selected Bands from TGA-FTIR Spectra of Neutrals from 450-650 °F Distillates of Coal Liquids.