

PRELIMINARY EXAMINATION OF COAL LIQUEFACTION PRODUCTS

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INTRODUCTION

The three direct general processes for converting coals to liquid fuels are: catalyzed hydrogenation, staged pyrolysis, and solvent refining (1,2). Each of these processes results in the production of a coal liquid which contains a variety of desirable and undesirable components. The desirable coal liquids are the oils-saturated and aromatic hydrocarbons plus nonpolar nonhydrocarbons, and the resins-polar nonhydrocarbons. The undesirable species are the asphaltenes and the carbene-high molecular weight highly aromatic solids, and the carboids-polymerized coke-like materials. The undesirable elements: metals, sulfur, nitrogen, and oxygen are generally present in higher concentration in the asphaltene and carboid fractions. Under hydrogenolysis conditions, the conversion of coal to oil has been suggested to proceed via the following sequence (3): Coal \rightarrow Asphaltene \rightarrow Oil. Therefore, asphaltene generation and elimination are of great importance in the liquefaction process. A study of the chemical and physical properties of asphaltenes may lead to the discovery of ways to reduce or eliminate asphaltene build-up in coal liquids and to thereby increase the yields of desirable coal liquefaction products. In this work, coal liquids from representative liquefaction processes have been separated by solvent fractionation, and the fractions are being examined by various analytical and physical techniques. Particular attention is being directed toward asphaltene separation, purification and characterization.

RESULTS AND DISCUSSION

A solvent fractionation scheme for separating coal liquid products into five fractions (oil, resin, asphaltene, carbene, and carboid) is shown in Figure 1. Representative coal liquid samples produced via the three direct coal liquefaction processes were separated into the five fractions described above. The results are presented in Figure 2. For the catalyzed hydrogenation product produced in the Synthoil process (4), the product composition is about 61% oil, 22% resin, 13% asphaltene, 0.6% carbene, and 3% carboid. The staged pyrolysis filtered product* from the FMC Corporation's COED process (5) has a product composition of about 26% oil, 48% resin, 15% asphaltene, 1% carbene and 10% carboid. The solvent refined coal (SRC) produced by Catalytic Inc. based on PAMCO's SRC process (6) affords about 4% oil, 15% resin, 45% asphaltene, 2% carbene, and 34% carboid. The results found in this work are in good agreement with those reported recently for solvent fractionation of a Synthoil catalytic hydrogenation product, and a non-catalytic SRC product (7). These workers found for a Synthoil product, 80% pentane soluble material, 15% of pentane insoluble and benzene or toluene soluble material, and 5% of benzene insoluble material. For an SRC product they found 20%, 46% and 34% respectively for the above three fractions. They found their benzene insoluble fraction to be pyridine soluble, and named this fraction 'pre-asphaltene' in the belief that it might be intermediate between coal and classical asphaltene. We feel, however, that the benzene insoluble fractions may arise from reactive coal depolymerization moieties which are not stabilized by hydrogenation, but are repolymerized into materials more difficult to degrade than the original coal substance. More work will have to be done

*The filtered product is the pyrolysis product produced prior to the final hydro-treating reaction. The FMC-COED Syncrude produced by hydrotreating the filtered product at 3100psi, 775°F consists of about 99% oil, 0.8% resin, and 0.2% asphaltene.

to elucidate the origin of this fraction.

The analyses of the starting coal liquids and the various solvent fractions are given in Tables I, II, and III. Semiquantitative Metal Analyses are presented in Table IV. It may be seen that heteroatoms and metals are generally concentrated in the asphaltene and carboid fractions.

TABLE I. - Synthoil Solvent Fractions Ultimate Analysis, %*

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	87.26	8.44	0.94	0.10	3.26	0.69	
Oil	87.74	9.58	0.60	0.43	1.65	0.02	260
Resin	87.27	7.77	1.30	0.14	3.52	0.30	
Asphaltene	87.27	6.51	1.63	0.66	3.93	0.48	738
Carbene	87.96	5.94	1.72	0.74	3.64	0.56	
Carboid	88.32	5.69	1.64	2.07	2.28	8.80	

*Moisture and ash free

**By difference

***VPO in benzene

TABLE II. - FMC-COED Solvent Fractions Ultimate Analysis, %*, MW

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	83.04	7.68	1.09	1.11	7.08	0.28	
Oil	85.88	9.75	0.42	1.08	2.87	0.01	310
Resin	83.25	7.25	1.06	1.26	7.18	0.39	
Asphaltene	82.14	6.47	1.70	2.58	7.11	0.79	458
Carbene	81.17	6.01	1.69	1.31	9.82	0.11	
Carboid	78.47	5.65	1.95	1.85	12.08	1.31	

*Moisture and ash free

**By difference

***VPO in benzene

TABLE III. - Cat. Inc. SRC Solvent Fractions Ultimate Analysis, %*

Fraction	C	H	N	S	O**	Ash	MW***
Coal liquid	88.71	5.53	1.26	0.19	4.31	0.29	
Oil	90.99	6.94	0.41	0.57	1.09	0.25	
Resin	89.88	6.64	0.84	0.00	2.64	0.05	
Asphaltene	88.79	5.61	1.25	0.12	4.23	0.78	747
Carbene	89.77	5.03	1.11	0.26	3.83	0.40	
Carboid	87.08	4.70	0.96	0.34	6.92	0.71	

*Moisture and ash free

**By difference

***VPO in benzene

TABLE IV. - Semiquantitative Metal Analysis*

Major Elements	Synthoil		FMC-COED		Cat, Inc, SRC	
	Asphaltene	Benzene Insoluble	Asphaltene	Benzene Insoluble	Asphaltene	Benzene Insoluble
Si	180	1800	210	100	55	130
Fe	130	420	20	270	7	58
Al	8	760	57	140	6	420
Ti	69	130	12	10	1	71
B	60	77	81	72	5	18
Ca	3	69	39	280	26	96
Mg	1	29	5	14	10	140

*Results in ppm

Table V. shows the color indices (8) (integrated absorption of a species between 750nm and 400nm) of the various solvent fractions for different coal liquids. Since the color index of an aromatic molecule is a function of the size of the aromatic π -system, it appears reasonable to assume that the increase in the color indices in going from oil, to resin to asphaltene to carbene, reflects an increase in the size of the respective π -systems. The color indices and molecular weights of the carboid fractions have not been determined yet. However, as they are the darkest and most insoluble of the fractions it is expected that they will exhibit high color indices and molecular weights.

TABLE V. - Color Indices, I* of Solvent Fractions

Fraction	Synthoil	FMC-COED	Cat, Inc, SRC
Oil	0.1	0.1	0.4
Resin	1.7	1.8	1.5
Asphaltene	12.7	4.1	16.6
Carbene	24.7	5.3	48.5
Carboid	-	-	-

$$*I = \int_{400\text{nm}}^{750\text{nm}} \text{Ad}\lambda \text{ in THF}$$

Tables VI, and VII show the carbon aromaticities, f_a (9) and the hydrogen percentages by proton type (10) for asphaltenes produced in the different processes. Carbon aromaticities are found to be similar in the preliminary measurements.

The solvent refined coals yield asphaltenes which contain a higher percentage of aromatic protons relative to benzyl and saturated protons than do the other types of liquefied coals.

Asphaltenes produced in the Synthoil process have been reported to consist of acidic and basic components (11). These components have been separated by treating the asphaltenes, dissolved in toluene, with dry HCl gas. The basic component precipitates as an HCl adduct in 57% yield, and the acidic and neutral components (43%) remain in solution. In this work we have further separated asphaltenes into two major fractions by solvent elution chromatography. The two major fractions obtained by elution from silica gel with benzene and diethyl ether have different properties although they both may be freeze-dried to brown powders from benzene solutions.

Table VIII, gives the total weight % asphaltenes recovered, and the % distribution of asphaltenes obtained using the eluents benzene and diethyl ether. Table IX, compares the color indices of the solvent eluted fractions with those of the starting asphaltenes. The color indices for all the diethyl ether-eluted fractions are lower than either the starting asphaltenes or the benzene-eluted asphaltenes. This suggests

TABLE VI. - X-Ray Carbon Aromaticity, f_a^*

Samples	Asphaltene	Benzene Fraction	Diethyl Ether Fraction
Synthoil	0.49	0.43	0.39
FMC-COED	0.45	0.43	0.41
PAMCO SRC	0.48	0.48	0.52

$$*f_a = C_A/C_{total} = A_{002}/A_{002} + A_r$$

C_A = number of aromatic carbons

C_{total} = number of total carbons

A_{002} = area under peak for aromatic carbons

A_r = area under peak for saturated carbons

TABLE VII. - NMR H-Percentages By Proton Type*

Asphaltene	$H_{aromatic}$	H_{benzyl}^{**}	H_{sat}^{**}
Synthoil	33	42	25
FMC-COED	37	43	20
Cat. Inc. SRC	50	34	16
PAMCO SRC	45	38	17

*Run on Varian T-60 NMR, Solvent 99.8% $DCCl_3$ + 1% TMS

**Separation point between H_{benzyl} and H_{sat} chosen at $\tau = 8.27$

TABLE VIII. - Silica Gel Chromatography of Asphaltenes

Asphaltene Sample	Total Wt % Recovered	Wt % with Solvent	
		Benzene	Diethyl Ether
Synthoil	84	57	43
FMC-COED	88	38	62
Cat. Inc. SRC	89	66	34
PAMCO SRC	88	51	49

a less extensive π -aromatic structure in these fractions. A comparison of the analyses and molecular weights of the various silica gel chromatography fractions is presented in Table X. The H/C ratios are highest in the diethyl ether-eluted fractions suggesting relatively more aliphatic carbons in this fraction. Table VI also indicates the aromaticity of the diethyl ether fraction is generally lower than the benzene fraction, except the PAMCO sample which could be due to some odd effect. The percentages of the heteroatoms nitrogen and oxygen are also appreciably greater in the diethyl ether-eluted fractions. These results are consistent with the acidic nature of silica gel, and the expectation that silica gel would preferentially adsorb basic molecules. This suggests that silica gel chromatography may provide a mild, chlorine-free procedure for separating asphaltenes into basic and non-basic components.

Actually, the words 'acid' and 'base' as reported by Sternberg et al. (11,7) do not adequately classify or clarify the coal-derived asphaltene. We would suggest acceptor (π -deficient) and donor (π -abundant), since their association and the nature of charge transfer is well known in asphaltene (12). The asphaltene thus formed is a complex and not as a salt in the sense of ionizable species of acid or base. We feel the benzene-eluted fraction could be neutral, the ethyl ether-eluted fraction polar, and by properly selecting adequate solvent, another more polar fraction can also be obtained. All these phenomena can be explained on the basis of charge-transfer. Actually, the existence of different degrees of association of this charge-transfer makes the task of separation of asphaltene difficult.

TABLE IX. - Color Indices, I*, of Silica Gel Fractions

Sample	Asphaltene	Eluent	
		Benzene	Diethyl Ether
Synthoil	12.7	12.1	8.2
FMC-COED	4.1	5.1	3.5
Cat. Inc. SRC	16.6	13.4	10.7
PAMCO SRC	10.4	9.4	8.8

$$*I = \int_{400\text{nm}}^{750\text{nm}} \text{Ad}\lambda \text{ in THF.}$$

TABLE X. - Silica Gel Chromatography Fractions Ultimate Analysis, %*, and MW

Sample	C	H	N	S	O**	Ash	MW***
Synthoil Asph.	87.27	6.51	1.64	0.66	3.92	0.48	738
Benzene	89.15	6.57	0.58	0.99	2.71	0.97	614
Diethyl Ether	85.17	6.86	1.60	0.73	5.64	1.19	560
FMC-COED Asph.	82.14	6.47	1.70	2.58	7.11	0.79	458
Benzene	83.83	6.30	1.06	1.93	6.88	1.38	445
Diethyl Ether	79.67	6.48	1.54	1.33	10.98	1.23	340
Cat. Inc. Asph.	88.80	5.61	1.25	0.12	4.22	0.78	747
Benzene	87.66	6.40	0.65	0.65	4.64	1.01	467
Diethyl Ether	84.73	6.33	1.67	0.79	6.48	1.78	490
PAMCO Asph.	86.33	6.15	1.47	1.13	4.92	1.50	432
Benzene	87.27	6.20	0.68	1.20	4.65	1.83	421
Diethyl Ether	83.00	6.52	1.99	1.01	7.48	2.03	465

*Moisture and Ash free

**By difference

***VPO in Benzene

SUMMARY

A preliminary examination of coal liquefaction products from four different coal liquefaction processes has been carried out. Each coal liquid has been separated into five different fractions by solvent fractionation. Total recoveries ranging from 93 to 97% by weight have been obtained. These solvent fractions are respectively: oil, resin, asphaltene, carbene, and carboid. We have further separated the asphaltene fraction by utilization of solvent elution chromatography with silica gel, into two fractions of different polarities. Unlike the asphaltene separation method described by Sternberg et al. (11), which gives a high chlorine content (4.1-4.5%), the present method does not chemically alter the asphaltenes.

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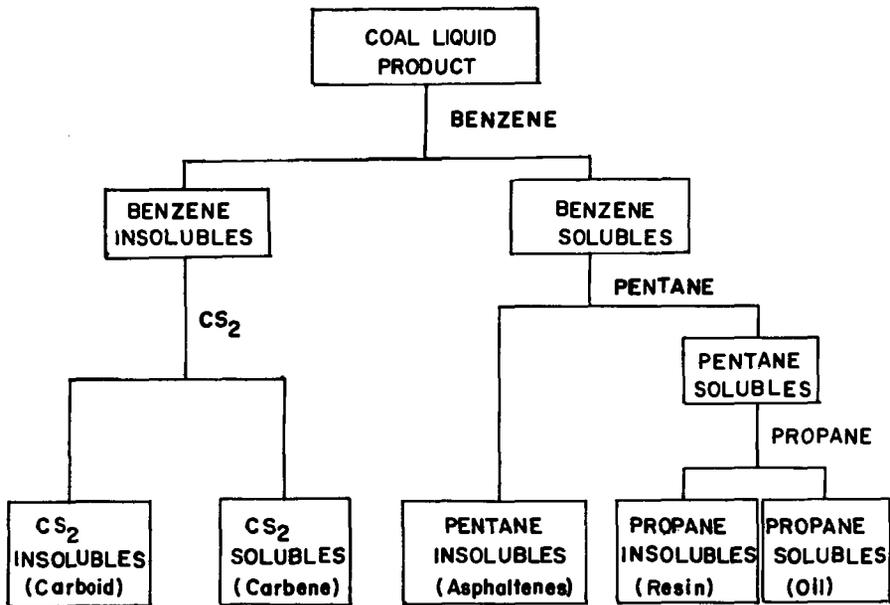


FIGURE 1 SOLVENT FRACTIONATION SCHEME FOR COAL LIQUID PRODUCT

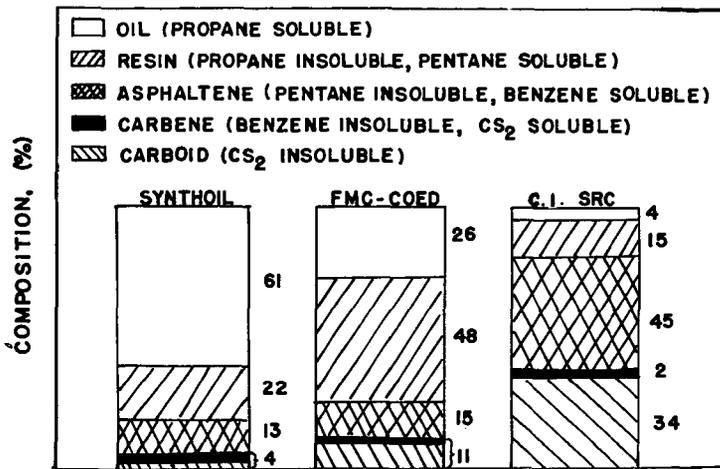


FIGURE 2 SOLVENT FRACTIONATION ANALYSIS OF COAL LIQUID PRODUCTS

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