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**CHEMISTRY AND STRUCTURE OF COAL DERIVED ASPHALTENES
AND PREASPHALTENES**

Quarterly Progress Report for October—December 1979

MASTER

Work Performed Under Contract No. EX-76-C-01-2031

University of Southern California
Los Angeles, California

U. S. DEPARTMENT OF ENERGY

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CHEMISTRY AND STRUCTURE OF COAL DERIVED ASPHALTENES AND PREASPHALTENES

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October to December, 1979

University of Southern California

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OBJECTIVE AND SCOPE OF WORK

It is the objective of this project to isolate the asphaltene and preasphaltene fractions from coal liquids from a number of liquefaction processes. These processes consist of in general: catalytic hydrogenation, staged pyrolysis and solvent refining. These asphaltene fractions may be further separated by both gradient elution through column chromatography, and molecular size distribution through gel permeation chromatography.

Those coal-derived asphaltene and preasphaltene fractions will be investigated by various chemical and physical methods for characterization of their structures. After the parameters are obtained, these parameters will be correlated with the refining and conversion variables which control a given type of liquefaction process. The effects of asphaltene in catalysis, ash or metal removal, desulfurization and denitrification will also be correlated. It is anticipated that understanding the role of asphaltenes in liquefaction processes will enable engineers to both improve existing processes, and to make recommendations for operational changes in planned liquefaction units in the United States.

The objective of Phase 1 was to complete the isolation and separation of coal liquid fractions and to initiate their characterization.

The objective of Phase 2 is to continue the characterization of coal asphaltenes and other coal liquid fractions by use of physical and instrumental methods. The structural parameters obtained will be used to postulate hypothetical average structures for coal liquid fractions.

The objective of Phase 3 is to concentrate on the characterization of the preasphaltene (benzene insoluble fraction) of coal liquid fraction by the available physical and chemical methods to obtain a number of structural parameters.

Inter-Conversion of Coal Liquid Fractions

The solvent refined coal liquid from the Pittsburgh & Midway Coal Mining Company pilot plant located at Fort Lewis, Washington, has been received and separated reproducibly by the standard solvent fractionation method (1) into three fractions. The coal liquid received is so-called stripper bottom product from SRC-II mode. Table I shows the coal liquefaction reaction conditions and the composition of the products. The fractionation scheme is shown in Fig. 1, while all the separation results are shown in Table II. This coal liquid contains 47.2% of pentane-soluble fraction (PS), 18.5% of asphaltene fraction (A), and 34.3% of benzene-insoluble fraction (BI). The recovery of the fractionation method is about 97.3%. These three fractions are kept for latter reaction experiments.

The 300 cc autoclave system equipped with injection loading, withdrawal systems, and the temperature controller, described before (2), was used as the reaction vessel in this quarter. In most reaction studies, tetralin was used as a transport vehicle oil. It was used also for donating hydrogen to the acceptor compounds. Nitrogen gas, instead of hydrogen, has been used for the pressure system, since this simplifies the reaction and gives a clearer picture for the reaction between reactants and solvent.

The conversion results on PS fraction at different conditions are shown in Table III, while the isothermal reaction results on it are in Table IV. With tetralin as a vehicle oil, the results show that only small or negligible amounts of PS are converted into A and BI fractions. However, when PS is pyrolyzed, 26% is polymerized into A and BI fractions. This indicates that tetralin can suppress the formation of A and BI fractions from PS. It is also noted that the composition of coal liquid may change during distillation because of the polymerization. Since A and BI are responsible for the high viscosity of the coal liquid, special care must be taken when the distillation column is designed for separation purpose. Further work is required in order to solve this problem.

The conversion results on A fraction at various conditions are shown in Table V. It indicates that 40 to 70 percent of A has been converted to PS or BI, depending on the temperature and pressure used. Run No. 9 in Table V is the conversion result of BI fraction. This result indicates that PS fraction was also formed from the BI fraction by conversion, in addition to the direct conversion from A. Table VI shows the results from isothermal conversion of A at 760° F. The distribution of the products from the above reactions is shown in Figure 2.

From the above results, the reaction scheme for the isothermal conversion can be rationalized as follows:

Table I Reaction Conditions and Product Composition of SRC II
Stripper Bottom

SAMPLE: SRC II Stripper Bottom

COAL: Pittsburgh Seam Coal, Blackville No. 2 Mine

TEMP : 862⁰ F

Pressure H₂ : 1909 psig

Run No. : MBR No. 12

Composition (%):

Naphtha: 0.11 (IBP to 350⁰ F)

Middle Dist.: 0.13 (350 to 550⁰ F)

Heavy Dist.: 43.94 (550 to 850⁰ F)

Vacuum Btms.: 55.80

Remark: 1.6% Pyridine Insolubles = 21.50

Figure 1 Solvent Fractionation Scheme

Table II Solvent Fractionation Analysis of SRC II Stripper Bottom

Wt. %			
<u>PS</u>	<u>A</u>	<u>BI</u>	<u>Recovery</u>
49.9	13.2	36.9	96.7
44.2	22.5	33.4	95.2
47.9	17.6	34.5	99.0
44.1	23.3	32.6	94.2
49.1	17.0	33.9	96.6
49.4	16.4	34.2	95.8
45.9	19.4	34.7	98.9
47.6	16.3	36.1	97.5
49.6	15.7	34.7	101.7
Ave: 47.2±3.1	18.5±4.8	34.3±1.8	97.3±3.1

TABLE III. Experimental Conversion Results on SRC II - PS

Run No.	Sample	Experimental Conditions					Product Distribution (Wt. %)			
		Temp. (°F)	Pressure (psi g)	Time (hr)	Tetralin to Sample Ratio	Reaction Recovery (%)	PS	Asphaltene	B.I.	Separation Recovery %
7	PS	750	700	24	5:1	96.8	99.0	<1.0	<0.1	97.4
8	PS	800	1900	24	5:1	95.1	99.0	<1.0	<0.1	94.2
2-8	PS	650	800	24	2:1	91.3	93.85	6.00	0.15	100.4
16	PS	710	900	2	0	-	73.4	22.8	3.8	91.2

TABLE IV. Isothermal Reaction Results on SRC II - PS

Temp. = 650° F ; Pressure = 800 psi g , Tetralin to Sample Ratio = 2:1 , Reaction Recovery: 91.3%

Run No.	Time (hr.)	<u>Product Distribution (Wt. %)</u>			<u>Separation Recovery %</u>
		<u>PS</u>	<u>Asphaltene</u>	<u>B.I.</u>	
2-1	0.5	97.0	1.2	1.8	74.4
2-2	1.0	95.4	1.8	2.8	82.7
2-3	2.0	92.6	4.6	2.9	88.2
2-4	3.0	94.4	4.1	1.5	94.0
2-6	5.0	96.0	2.5	1.5	95.9
2-7	24.0	95.2	3.5	1.3	97.5

TABLE V. Experimental Conversion Results on SRC II - Asphaltene and B.I.

Run No.	Sample	Experimental Conditions				Reaction Recovery(%)	Product Distribution (Wt.%)			Separation Recovery (%)
		Temp. (°F)	Pressure (psig)	Time (hr)	Tetralin to Sample ratio		PS	Asphaltene	B.I.	
3	Asphaltene	650	1800	24	5:1	90.9	42.1	38.5	19.5	----
13-3	"	710	700	24	5:1	96.8	48.9	35.8	15.3	96.7
5	"	760	1800	24	5:1	77.4	69.8	30.2	0.1	94.3
9	B.I.	800	1800	17	5:1	92.0	7.3	4.8	87.9	97.3

Table VI. Isothermal Reaction Results on SRC 11 - Asphaltene at 760°F

Pressure: 700psig; Tetralin to Sample Ratio=5:1

Run No.	Time (hr)	Product Distribution(Wt.%)			Separation Recovery(%)	Reaction Recovery(%)	Conversion(%) (100%-A%)
		PS	A	BI			
17-1	0.25	49.33	44.24	6.43	97.95		55.76
17-2	0.50	51.48	42.51	6.01	97.14		57.49
17-3	0.75	49.11	43.90	6.99	96.91	97.24	56.10
17-4	1.00	48.21	44.91	6.88	96.03		55.09
17-5	1.50	48.13	44.72	7.14	96.68		55.28
18-1	1.50	49.91	42.81	7.28	97.39		57.19
18-2	2.0	48.14	43.57	8.29	97.01	92.69	56.43
18-3	3.0	52.21	48.86	3.93	99.92		56.14
19-1	5.0	72.96	24.50	2.55	95.96		75.50
19-2	7.0	77.13	21.60	1.27	94.66		78.40
19-3	10.0	77.22	18.90	3.83	96.28	106.58	81.10
19-4	22.0	85.69	12.61	1.70	94.01		87.39

Fig. 2. Product Distribution on Asphaltene at 760° F, 700 psig

From (i), it is clear that A can be converted into PS and BI through two parallel reaction routes by decomposition reaction accompanied with the polymerization reaction, for the first stage of the conversion. Generally, decomposition is much faster than the polymerization reaction. At this condition, the formation of BI by polymerization of A reaches a maximum, then decomposition reaction into PS directly initiates. For the second stage of the conversion process, it is followed by the further decomposition of A into PS.

It has been reported as a first order reaction for the coal conversion process previously (3,4). A mechanism such as (ii)

represents the kinetic model. Due to the presence of tetralin, the PS fraction formed in the first stage does not polymerize in the later stage of the conversion reaction. The decomposition reaction in the first stage is the one that was observed in the previous literatures (3,4). This is the first time that the secondary decomposition reaction has been discovered experimentally. In the previous studies (3,4), the BI fraction has never been mentioned, and this is the first time that the reaction kinetics among those three fractions has been studied.

A detailed studies of this reaction at different temperatures would shed light to confirm the kinetic mechanism (i) as we have proposed. Attempt has been initiated for the above tests incorporated with a computer modeling of the kinetics to be tested to match with the experimental results.

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