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MASTER

HYDROGEN BONDING IN ASPHALTENES
AND COAL LIQUIDS

Quarterly Report for the Period
August 1, 1982 - October 31, 1982

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Objective and Scope of Work

The objective of this project is to investigate the nature and strength of hydrogen bonding and other molecular interactions in coal liquids and their fractions. Determinations are made of the molecular interactions involving the preasphaltenes, asphaltene, and oil fractions, together with their separated sub-fractions, obtained from coal liquids after hydroprocessing under different processing conditions and accelerated aging. NMR, IR, GC/MS, GPC, ESR, calorimetric and viscometric methods are used to determine structural changes caused by upgrading and aging of coal liquids.

Contract DE-AC 22-80 PC 30252 on Hydrogen Bonding in Asphaltenes and Coal Liquids was awarded to Duquesne University for the years August, 1980 to July, 1983. This is the ninth quarterly report, for the period August 1, 1982 to October 31, 1982. The following paper, on Analysis of Upgraded SRC-II and H-coal liquid products, by L.J.S. Young, N.C. Li, and D. Hardy, was presented at the Kansas City ACS Meeting, September, 1982 and has been accepted for publication by Fuel.

ABSTRACT:

Upgraded coal-derived liquids obtained from catalytic hydroprocessing of SRC-II and H-coal syncrudes have been studied by IR, PMR, GC/MS, and silica gel chromatography. With increase in residence time, nitrogen, oxygen, and aromatics decrease, accompanied by a large increase in naphthenes. Negligible hydrogen-bonded material was found in the upgraded liquids. All the upgraded liquids show low viscosity at 298 K ($1.3\text{--}1.4\text{ mNsm}^{-2}$), even though saturate and aromatic fractions varied with processing severity. In the aromatic-I fraction, 1-ring aromatics increase, and 3-ring aromatics decrease, with an increase in severity of hydroprocessing. GC/MS analyses indicate a remarkable qualitative similarity for saturate and aromatic fractions irrespective of syncrude source. Only the heavier end of the aromatic-I fraction is noticeably different. Tentative identifications are made for most of the significant components based on mass spectra and GC retention times. 600-MHz PMR spectra of the upgraded SRC-II and H-coal liquids look identical, but NMR difference technique showed slight differences in concentrations of certain species between the two liquids.

INTRODUCTION

Interest in catalytic hydroprocessing of coal-derived liquids has intensified in recent times because of the need to convert heavy feeds to more useful fuels for transportation use. Analytical data on upgraded liquids—physical and chemical characteristics such as specific gravity, aniline point, heteroatom content (O,N,S)— are of importance in determining the process parameters which control the product composition and product properties. The purpose of this study was to analyze upgraded SRC-II and H-coal liquids provided by the Chevron Research Co. IR,NMR,GC, GC/MS, and silica gel chromatography were applied with the objective of obtaining a better understanding of coal liquid refining processes.

EXPERIMENTAL

SRC-II process products were made from Pittsburgh Seam (Elacksville No. 2 Mine) at Pittsburgh and Midway Coal Co. These products were blended in the ratio recommended by the DOE Technical officer to represent a typical net whole liquid product from the SRC-II process. The blend is referred to as SRC-II syncrude. H-coal process products derived from Illinois No. 6 coal were blended in the ratio recommended by Hydrocarbon Research Inc. to represent a net whole liquid process product from the H-coal process. This blend is referred to as H-coal syncrude.

Two samples of SRC-II syncrude and three samples of H-coal syncrude were hydrotreated using Chevron's ICR 106 catalyst (containing nickel,tungster,silica and alumina) at 672 K and approximately 15.6 MPa H_2 partial pressure.

NMR spectra were obtained with a 600-MHz NMR spectrometer or a 60-MHz FT-NMR (Hitachi Perkin-Elmer) spectrometer with TMS as the internal reference. IR spectra were recorded from neat samples on NaCl plates as thin films on a Beckman IR-20 infrared spectrometer. GC profiles were obtained with a Hewlett-Packard Model 5700A equipped with a flame ionization detector and Sigma-10 data system. Capillary methyl silicone (length 12 m) and methyl phenyl silicone (length 30 m) columns were used. The GC/MS analysis was performed on a SP-2100 fused silica capillary column (length 50 m) interfaced directly into a Hewlett-Packard 5982 MS at 70 eV.

Two neutral fractions of the coal-derived liquids were obtained by treating the SRC-II and H-coal syncrudes with IRA-904 anion-exchange resin and then with Amberlyst-15 cation-exchange resin to remove acid and base fractions, respectively. The ion-exchange resins were purchased from Rohm and Haas and were activated according to the method described by Jewell, et al.¹ The neutral fractions of the syncrudes and the upgraded coal-derived liquids were separated into saturate, aromatic-I and aromatic-II fractions by silica gel chromatography. A 1.2 x 105 cm column was packed with 64 g of silica gel which had been activated by heating for 16 h at 353 K in a vacuum oven. A 2 g quantity of the neutral fraction or upgraded liquid was dissolved in pentane and charged to the column. The saturate fraction was eluted with pentane until the uv absorbance of the eluate at 270 nm equalled 0.05. Aromatic-I and aromatic-II fractions were eluted with CHCl₃ and methanol, respectively, until the uv absorbance at 270 nm reached about zero.

RESULTS AND DISCUSSION

The hydroprocessing conditions, elemental analysis and physical properties of the feeds and upgraded liquids are listed in Table 1. Apparently, the type of coal and hydrotreatment contact time greatly influence these properties. The contact time is the reciprocal of the liquid hourly space velocity (LHSV, in $\text{cm}^3 \text{ feed/h cm}^3 \text{ catalyst}$).

Infrared spectra of the coal-derived liquids (Figure 1 for H-coal, Figure 2 for SRC-II) show differences in aliphatic stretching bands at 2920 and 2960 cm^{-1} for CH_2 and CH_3 , respectively, and aromatic C-C and/or hydrogen-bonded carbonyl stretching at 1610 cm^{-1} . The aromatic stretching at 3020 cm^{-1} decreases with increasing severity (decrease in LHSV) of hydrotreating. The syncrudes show an obvious broad peak centered at 3400 cm^{-1} which is ascribed to the hydrogen-bonded OH and NH structures. However, a negligible hydrogen-bonded structure was found in upgraded liquids. The neutral fraction, an acid- and base-free fraction, shows a similar absorption to the upgraded liquids.

NMR spectra (Figure 3 for SRC-II liquids) show that the aromatic protons decrease with decrease in LHSV (increasing severity of hydroprocessing). The aromatic protons of the upgraded coal liquids appearing in the range 6.5 to 7.2 ppm indicate that the upgraded liquids contain mostly one or two ring aromatics. The sharp singlet at 1.44 ppm is due to cyclohexane which indicates that the content of naphthene in the upgraded liquids is appreciable. This is consistent with data in Table 1, which lists naphthene contents in the range 57.2 to 89.9% (liquid volume %).

Molecular parameters were determined from the PMR data using the Brown and Ladner equations^{2,3}. Hydrogen was divided into the following four types: aromatic hydrogen (H_a), 5-9 ppm; hydrogen attached α to an aromatic carbon (H_α), 2-4 ppm; hydrogen bound to β atoms or further from the aromatic rings except for terminal methyl (H_β), 1.1-2 ppm; and hydrogen in terminal methyl (H_γ), 0.3-1.1 ppm. The proton distribution of the syncrudes and their upgraded liquids is listed in Table 2. It is seen that the aromatic hydrogen content decreases with increase in contact time. The increase in aliphatic hydrogens occurs at the position β or further away from the aromatic ring, H_β or H_γ and is accompanied by a decrease in H_α . The increase of H_β in upgraded liquids is primarily due to the increase of naphthene content.

The viscosity of the syncrudes and their upgraded liquids was measured by an Ostward¹ type viscometer at 298 K. The data are given in Table 1. Since the contents of heteroatoms are in the range of only a few ppm and the hydrogen-bonded structure is negligible, the upgraded liquids all have low viscosity, ranging only from 1.25 to 1.40 mNsm⁻². This is in spite of some variation in the saturate and aromatic contents. The viscosities of SRC-II and H-coal syncrudes are 2.74 and 2.04 mNsm⁻², respectively.

In order to characterize the composition of the upgraded samples, silica gel chromatography was employed to separate the coal liquids into saturate and aromatic fractions, and the content of each fraction is listed in Table 3. It is seen that the saturate fraction

content increases with contact time, accompanied by a decrease in aromatic fractions. The neat IR spectrum of the saturate fraction derived from 1.0 LHSV H-coal shows the absence of absorptions at 3020-3080 cm^{-1} and 1600 cm^{-1} , indicating that the saturates are not contaminated by aromatic fractions. The recoveries were determined gravimetrically and range between 94 and 99.8%, indicating that the method used for separation of upgraded coal liquids is appropriate. The saturate content of high severity hydrotreated liquids, 0.5 LHSV, is dramatically increased from 15.1 to 92.9 wt % and from 28.8 to 73.8%, for SRC-II and H-coal, respectively.

The saturate and aromatic-I fractions were studied by GC using methyl silicone and methyl phenyl silicone capillary columns, respectively. The temperature programs used for saturate and aromatic-I fractions were from 293 K (2 min) to 433 K (4 min) by increasing rate at 2° per min., and from 343 K to 540 K by increasing rate at 2° per min., respectively. The severity of hydrotreating seems not to affect the types, only the concentration of compounds in both the saturate and aromatic-I fractions.

A new retention index system for programmed-temperature capillary column gas chromatography has been reported for polycyclic aromatic hydrocarbons using naphthalene, phenanthrene, chrysene, and picene as internal standards⁴. Several aromatic model compounds have been studied under the same experimental conditions but using a 30 m. of methyl phenyl silicone column instead of 12 m. Unfortunately, most of the experimental retention indices of aromatics are out of the range of deviation compared with the data of Lee, et al.⁴ However, an approximate quantitative analysis of aromatics based on the ring-number can be

obtained by using the internal standards of naphthalene and phenanthrene since most of the compounds that appear before naphthalene, between naphthalene and phenanthrene, and after phenanthrene are 1-, 2-, and 3-ring aromatics, respectively. The more severely upgraded coal liquids contain more 1-ring and less 3-ring aromatic compounds, compared to the syncrude and the less severely upgraded coal liquids.

We have obtained GC/MS total ion chromatograms of the saturate fractions (Fig. 4) and the aromatic fractions (Fig. 5) of upgraded SRC-II and H-coal. The total ion chromatograms are normalized to the most intense peak in each spectrum. By matching retention times and mass spectra of the numbered peaks, we observe a remarkable similarity for each fraction irrespective of whether the source is SRC-II or H-coal. Only the heavier end of the aromatic-I fraction is noticeably different. The tentative identifications^{5,6} of the numbered peaks in Figures 4 and 5 are given in Tables 4 and 5. In comparing the chromatograms of Fig. 4, the concentrations of the following species are greater in SRC-II (LHSV 1.5) than in H-coal (LHSV 1.5): C₆-cyclohexanes, C₇-cyclohexanes, C₈-cyclohexanes, dimethyl tetralins, n-decane, n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, and n-heptadecane, whereas the H-coal saturate fraction contains greater concentrations of the following: C₃-cyclohexanes, C₄-cyclohexanes, C₅-cyclohexanes, and trans-hexahydroindane. In comparing the GC/MS chromatograms of the aromatic-I

fractions of H-coal (LHSV 1.0) and of SRC-II (LHSV 1.5), the concentrations of the following species are greater in H-coal than in SRC-II: C_3 -benzenes, C_7 -benzene, C_8 -benzenes, C_6 -indane or C_5 -tetralin, indane, and methyl indane. The concentration of C_6 -benzenes is greater in SRC-II (LHSV 1.5) than in H-coal (LHSV 1.0) aromatic-I fractions.

600-MHz PMR spectra of the upgraded SRC-II and H-coal liquids (both 1.5 LHSV) took identical. We have applied the NMR difference technique⁷ to obtain differences in concentration of certain species between the two liquids. The difference spectrum was obtained from the individual proton spectra recorded under the same operational conditions in $CDCl_3$. The upgraded SRC-II liquid contains larger amounts of compounds which have CH_2 or CH groups ~~d~~ to the aromatic rings.

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Legends of figures

Fig. 1 Neat IR spectra of H-coal syncrude and its upgraded liquids

2 Neat IR spectra of SRC-II syncrude and its upgraded liquids

3 NMR spectra of SRC-II syncrude and its upgraded liquids

4 GC/MS chromatograms for the saturate fractions of (a) upgraded SRC-II, 1.5 LHSV, and (b) upgraded H-coal, 1.5 LHSV. Numbered peaks are tentatively identified in Table 4.

5 GC/MS chromatograms for the aromatic-I fractions of:

(a) 1.0 LHSV H-coal and (b) 1.5 LHSV SRC-II.

Numbered peaks are tentatively identified in Table 5.

Fig. 4

Fig. 5

Table 1. Properties and analysis of SRC-II and H-coal syncrudes
and their upgraded liquids*

Feed Sources	SRC-II			H-coal			
	Syncrude	LHSV, h ⁻¹		Syncrude	LHSV, h ⁻¹		
		1.5	0.5		1.5	1.0	0.5
Specific gravity, °API	18.6	34.1	39.3	25.8	33.1	35.9	36.2
Viscosity (cp) 298 K	2.74	1.25	1.25	2.04	1.40	1.34	1.39
Aniline point, °F	< 30	67.5	116.9	< 32	75.7	101.3	110.5
Total nitrogen, ppm	8,500	20	0.25	4,600	11.6	1.1	0.5
Oxygen, ppm	37,900	630	40	18,000	160	110	120
Sulfur, ppm	2,900	5	5	3,200	16		8.4
Hydrogen, wt %	10.46	12.4	13.7	11.39	12.3	12.8	13.2
Carbon, wt %	86.41			86.96			
Group type, LV %							
Paraffins		7.8	6.4		3.3	2.8	2.7
Naphthenes		57.2	89.9		58.6	73.2	84.0
Aromatics		35.0	4.3		38.1	23.0	13.2

* Received from Chevron Research Co.

Table 2 Proton distribution of coal liquids (area %)

	H _a (9-5 ppm)	H _α (4-2 ppm)	H _β (2-1.1 ppm)	H _γ (1.1-0.3 ppm)
S.C-II Syncrude	25.28	24.94	31.63	18.14
SRC-II 1.5 LHSV	8.52	13.74	47.92	29.82
SRC-II 0.5 LHSV	3.33	3.22	54.94	38.52
H-coal Syncrude	15.99	20.58	41.26	22.17
H-coal 1.5 LHSV	7.85	13.01	49.03	30.11
H-coal 1.0 LHSV	5.50	8.79	55.62	30.03
H-coal 0.5 LHSV	4.81	7.48	54.70	33.01

Table 3 Composition of coal liquids (Wt %)

	<u>Saturate</u>	<u>Aromatic-I</u>	<u>Aromatic-II</u>	<u>Recovery</u>
SRC-II Syncrude	15.1	80.2	4.0	99.3
SRC-II 1.5 LHSV	50.6	44.9	1.0	96.5
SRC-II 0.5 LHSV	92.9	5.1	0.8	98.8
H-coal Syncrude	28.8	66.3	3.7	99.8
H-coal 1.5 LHSV	53.2	30.6	15.6	99.6
H-coal 1.0 LHSV	68.0	23.3	2.7	94.0
H-coal 0.5 LHSV	73.8	22.0	3.4	99.2

Table 4 Tentative GC/MS identification of numbered peaks in Fig. 4
(Saturate fraction of upgraded liquids)

Peak No.	Tentative identification	Peak No.	Tentative identification
1	n-hexane	33	C ₅ -cyclohexane
2	cyclohexane	34	C ₅ -cyclohexane
3	methyl cyclohexane	35	C ₆ -cyclohexane
4	toluene (contaminant)	36	C ₆ -cyclohexane
5	dimethyl cyclohexane	37	C ₆ -cyclohexane
6	n-octane	38	C ₆ -cyclohexane
7	dimethyl cyclohexane	39	n-dodecane
8	ethyl cyclohexane	40	dimethyl decalin
9	C ₃ -cyclohexane	41	dimethyl decalin
10	C ₃ -cyclohexane	42	C ₆ -cyclohexane
11	n-nonane	43	C ₃ -decalin
12	branched C ₉ alkane	44	C ₃ -decalin
13	C ₃ -cyclohexane	45	C ₇ -cyclohexane
14	C ₃ -cyclohexane	46	C ₇ -cyclohexane
15	trans-hexahydroindane	47	n-tridecane+C ₇ -cyclohexane
16	C ₄ -cyclohexane	48	C ₃ -decalin
17	C ₄ -cyclohexane	49	C ₃ -decalin
18	C ₄ -cyclohexane	50	C ₈ -cyclohexane
19	n-decane	51	C ₈ -cyclohexane
20	C ₄ -cyclohexane	52	C ₈ -cyclohexane
21	C ₄ -cyclohexane	53	C ₈ -cyclohexane
22	C ₄ -cyclohexane	54	n-tetradecane
23	C ₄ -cyclohexane	55	C ₈ -cyclohexane
24	C ₅ -cyclohexane	56	C ₈ -cyclohexane
25	trans-decalin+C ₅ -cyclohexane	57	n-pentadecane
26	C ₅ cyclohexane	58	C ₅ -decalin
27	C ₅ cyclohexane	59	n-hexadecane
28	?	60	M.W. 220 (C ₃ phenanthrene?)
29	cis-decalin+C ₅ -cyclohexane	61	n-heptadecane
30	n-undecane	62	M.W. 234 (C ₄ phenanthrene ?)
31	cis-methyl decalin	63	n-octadecane
32	alkyl substituted decalin	64	n-nonadecane

Table 5 Tentative GC/MS identification of numbered peaks in Fig. 5
(aromatic-I fraction of upgraded liquids)

Peak No.	Tentative identification	Peak No.	Tentative identification
1	methylene chloride (contaminant)	25	methyl indane
2	toluene (contaminant)	26	tetralin
3	carbon tetrachloride(contaminant)	27	C ₆ -benzene
4	ethyl benzene	28	C ₆ -benzene
5	o- + p-xylene	29	C ₆ -benzene
6	m-xylene	30	C ₆ -benzene
7	C ₃ -benzene	31	C ₂ -indane or C ₁ -tetralin
8	C ₃ -benzene	32	C ₆ -benzene
9	C ₃ -benzene	33	C ₆ -benzene
10	C ₃ -benzene	34	C ₇ -benzene
11	C ₃ -benzene	35	C ₂ -indane or C ₁ -tetralin
12	C ₃ -benzene	36	C ₇ -benzene
13	C ₃ -benzene	37	C ₇ -benzene
14	C ₄ -benzene	38	C ₇ -benzene
15	C ₄ -benzene	39	C ₇ -benzene
16	indane	40	C ₄ -indane or C ₃ -tetralin
17	C ₄ -benzene	41	C ₄ -indane or C ₃ -tetralin
18	C ₄ -benzene	42	C ₈ -benzene
19	propenyl toluene	43	C ₄ -indane or C ₃ -tetralin
20	C ₅ -benzene	44	C ₄ -indane or C ₃ -tetralin
21	C ₅ -benzene	45	C ₅ -indane or C ₄ -tetralin
22	methyl indane	46	C ₆ -indane or C ₅ -tetralin
23	methyl indane	47	C ₆ -indane or C ₅ -tetralin
24	methyl indane	48	C ₆ -indane or C ₅ -tetralin
		49	?

Work in Progress:

Storage stabilities for an upgraded coal liquid (H-coal) were studied using laser light-scattering measurements with added 2,5-dimethylpyrrole (DMP) at the 200 ppm nitrogen (N) concentration. Three hydrotreated H-coal samples, produced at LHSV's of 0.5, 1.0, and 1.5 hr^{-1} by Chevron, were used in these tests. The three coal liquids contained 0.5, 1.1 and 11.6 ppm N, respectively. The most severely treated H-coal (LHSV 0.5 hr^{-1}) gave an S-shaped curve for light-scattering intensity as a function of storage time at room temperature. Our results show that the amount of DMP sediment formed on storage at 80⁰ and 120⁰C, and the extent of increase in light scattering at ambient temperature, increase with increase in LHSV. The DMP sediments of upgraded H-coal have been studied by solid-state (magic-angle spinning) C-13 NMR and ESCA techniques, and clear evidence has been obtained that oxygen is incorporated in the form of ether, carboxylate and carbonyl groups. Elemental analyses of the DMP deposits of upgraded H-coal give the formula $\text{C}_7\text{H}_8\text{NO}_{1.3}$. This suggests that DMP, $\text{C}_6\text{H}_9\text{N}$, predominates in the deposits with oxygen from the atmosphere incorporated. For the upgraded H-coal, 0.5 LHSV, in the presence of phenol, pyridine, and copper, we have found a positive synergistic effect between the oxygen- and nitrogen-containing compounds in promoting deposit formation and light scattering of the liquid fuel.