255
3-3-81
JWA

MASTER

(2)

Dr. 2369

DOE/PC/30252-T1

NTIS-25
Birn-181

HYDROGEN BONDING IN ASPHALTENES AND COAL LIQUIDS

Quarterly Report for Period Aug. 1-Oct. 31, 1980

By
N. C. Li
L. Jones
N. F. Yaggi

Work Performed Under Contract No. AC22-80PC30252

Duquesne University
Department of Chemistry
Pittsburgh, Pennsylvania

U. S. DEPARTMENT OF ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

HYDROGEN BONDING IN ASPHALTENES
AND COAL LIQUIDS

Quarterly Report for the period
Aug. 1, 1980 - Oct. 31, 1980

N.C. Li, L. Jones and N.F. Yaggi
Department of Chemistry, Duquesne University
Pittsburgh, PA 15219

Prepared for
The U.S. Department of Energy
Under Contract No. AC 22-80 PC 30252

mf

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 preasphaltene, asphaltene and oil, together with their separated fractions, obtained from coal liquids after hydroprocessing under different processing conditions and accelerated aging. NMR, IR, GC/MS, calorimetric, GPC, ESR, viscosity 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 has been awarded to Duquesne University for the period Aug. 1980-July, 1983. This is the first quarterly report, and describes the work accomplished from Aug. 1, 1980 to Oct. 31, 1980. During this period, a manuscript has been completed, with the title: 600-MHz Proton Magnetic Resonance Study of Coal-Derived Liquids, by T. Hara, K.C. Tewari, N.C. Li, F.K. Schweighardt. The paper is as follows:

ABSTRACT: The newly developed 600 MHz ^1H NMR Spectrometer is used to characterize coal-derived liquids and their chromatographically separated fractions. The distinct and well resolved proton resonance lines in both aromatic and aliphatic regions and IR analysis have been used to identify the major compounds and compound types. Double resonance technique has been applied for the chemical shift identification of donor protons ($\alpha\text{-CH}_2$, $\beta\text{-CH}_2$) of partially hydrogenated polynuclear aromatic compounds. An NMR difference technique is applied to determine specific compositional changes in upgraded liquids derived under identical process conditions, but from different coal sources.

Introduction

High resolution proton nuclear magnetic resonance (^1H NMR) spectrometry has been used as one of the major spectroscopic tools for chemical characterization on coal-derived materials, since Friedel (1) and Brown et al. (2) reported ^1H NMR spectra of coal-derived asphaltene and low-temperature vacuum carbonization products. Based on the quantitative proton distribution data, structural information for complex mixtures of coal-derived materials has been obtained using the Brown and Ladner equations (3) as well as the modified equations reported elsewhere (4-6). The higher-field NMR spectrometer (220 MHz) was applied to tar component by Bartle et al. (7). The proton resonance signals of coal-derived materials were divided into eleven ranges of chemical shift values and the signals in each range were assigned to various types of hydrogen by the addition of pure compounds. Schweighardt et al. used a 250 MHz NMR spectrometer for characterization and to quantify hydroxyl groups in coal-liquefaction oils and asphaltenes (8). Hydroxyl groups in coal-derived materials were converted into trimethylsilyl ethers and proton signals in methyl groups attached to silicon were measured. The well-resolved NMR spectra enabled them to characterize the nature of the original hydroxyl groups in coal-derived materials.

In the present study, 600 MHz ^1H NMR spectrometer working at 140.9 Kgauss is used for the characterization of solvent-refined coal liquid products (SRC-II) and their chromatographically separated subfractions. The assignment of well-resolved resonance lines becomes simpler by use of the highest magnetic field possible today to identify major compounds and compound types found in coal-liquids. A double resonance technique has been used for chemical shift identification of $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ protons attached to aromatic ring

structures. An NMR difference spectroscopic technique is used on a pair of coal-liquid samples to determine compositional change between them. Such quick and direct characterization without fractionation may help to assess the slight variation of process parameters in coal-liquefaction processes.

Experimental

A liquid solvent-refined coal product (SRC-II) was made from Western Kentucky bituminous coal at the Fort Lewis SRC pilot plant, having an initial boiling point of 453 K and an end boiling point of 665 K. The coal-liquid product was fractionated using ion-exchange and silica-gel chromatography (9-11). Amberlite IRA-904 and Amberlyst A-15 were used as anion and cation-exchange resins, respectively. Activation of the resins and silica-gel was performed by the method described by Jewell et al. (9). The ratios of the coal-liquid to the ion-exchange resins and silica-gel were 1:5 and 1:150 by weight, respectively. The SRC-II middle distillates, boiling point range of 450-565 K, used were from three different coals (Illinois No. 6, Western Kentucky 9/14 and Pittsburgh Seam) derived under the same process conditions, namely hydrogen pressure 13.8 MPa, reactor temperature 730 K, and a residence time of 1 hr.

The 600 MHz ^1H NMR spectrometer working at 140.9 kgauss has been developed by Bothner-By and Dadok at Carnegie-Mellon University (12). The resolution determined by half-height width of ethanol triplet was 0.41 Hz, and signal to noise ratio for a single scan was better than 500. Tetramethylsilane was used as a lock signal as well as for an internal standard. Each spectrum recorded was the result of 10-100 time-average scans in CDCl_3 solutions. The difference spectrum between the two SRC-II middle distillates was obtained from the individual proton spectrum recorded under the same concentration (38.2 g/l in CDCl_3) and operational conditions.

Infrared spectra were recorded in carbon tetrachloride in 5 mm KBr liquid cells or as a thin film between NaCl plates on a Beckman IR-20 infrared spectrometer. The number-average molecular weights were determined by vapor pressure osmometry in methylene chloride solutions (3-8 g/l) (13).

Results and Discussion

SRC-II liquid, boiling range of 453-665 K, was fractionated by solvent extraction based on its solubility in n-pentane. The pentane-soluble oil fraction (A) 99.3% of SRC-II, was further fractionated by sequential treatment with anion-exchange resin, cation-exchange resin and silica-gel column, as illustrated in Fig. 1. Weight percent yields of the fractions, relative to A are included in Figure 1.

After the treatment of Fraction A with anion-exchange resin, the non-reactive portion, acid-free fraction (B), did not exhibit absorptions characteristic of either phenolic OH or acidic NH stretching at 3,600 and 3,480 cm^{-1} , respectively. This indicates that compounds containing not only phenolic OH group but also acidic NH group can be removed by the reaction with anion-exchange resin, as has been suggested by Scheppele et al. (10). 600 MHz NMR spectra of the fractions A and B are shown in Fig. 2. Removal of the acidic fraction from A results in a complete disappearance of aromatic proton signals in the range 6.42-6.77 ppm. It is known that aromatic protons show upfield shift when electron-donating groups such as hydroxy group are attached to the same ring structure. It is interesting to note that aliphatic protons in the range of 2.20-2.30 ppm assigned to $-\text{CH}_3$ protons directly attached to mono-aromatic ring structure (14), also decreased drastically after the removal of acidic fractions.

Acidic and basic fractions adsorbed on the resins were recovered by sequential elution with different solvent systems, as shown in Fig. 1. Elemental analysis, molecular-weight, and empirical formula of fraction A and four major fractions (C, D, E and G), are summarized in Table 1. The results indicate that acidic fractions, particularly Acid-II (D), have lower molecular weights and neutral fraction (E) contains no significant amount of heteroatoms per molecule. On an average, Acid-II has one oxygen atom and no nitrogen per molecule. Base-II(G) has one nitrogen atom and negligible amount of oxygen in an average molecule. It should be noted that Acid-I (C) contains oxygen and nitrogen functionalities and that total number of oxygen and nitrogen atoms in an average molecule is close to one. The results may suggest that acidic fraction (C) is a mixture of oxygen-containing and nitrogen-containing compounds. The results on the heteroatom functionalities in Table 1 are well supported by solution infrared spectra of the fractions shown in Figure 3. Table 2 lists the percent distribution of heteroatoms among the fractions, calculated from the data in Table 1. We find 80% of the total oxygen located in two acidic fractions (C and D), and 49% of the total nitrogen are in Base-II (G) in spite of its low content (6.6%). Sulfur is distributed more evenly among the fractions, but higher in neutral fraction (E) and lower in acidic fractions C and D.

Figure 4 shows the boiling-point distribution, simulated by gas chromatography (ASTM D2887) for the major fractions E, C, D, and G. Fractions C, E and G give almost the same distribution curves, although G contains larger amount of higher boiling-point compounds than C. On the other hand, fraction D consists of lower boiling-point compounds which are concentrated in a more narrow range of boiling-point, i.e., 75% of D boils in the range of 461 to 516 K (370-470 F).

Neutral fraction (E) was further separated into saturate and aromatic fractions (Fig. 1). Fig. 5 shows neat infrared spectra of saturate fraction J and aromatic fraction K. Their characteristic absorptions are simple and all of the main absorptions can be assigned. For example, the absorption of 1380 cm^{-1} in fraction J can be assigned as symmetrical bending vibration of methyl group. Judging from the shape of the absorption, we can conclude that isopropyl or t-butyl groups are not the main functionalities with regard to methyl groups in this fraction. As for the aromatic fraction (K), several modes of carbon-carbon skeleton vibration can be found in the range of $1610\text{--}1450\text{ cm}^{-1}$, being partly overlapped with bending vibrations of CH_3 and CH_2 groups at about 1460 cm^{-1} (15).

The 600 MHz NMR spectrum of saturate fraction J (Fig. 6) shows a triplet at 0.89 ppm ($J = 6.5\text{ Hz}$) and a relatively sharp singlet at 1.26 ppm. The signal at 7.27 ppm is due to solvent impurity, chloroform. The result combined with the infrared spectrum shows that J is substantially composed of n-alkanes of high carbon numbers (16). Fig. 7 shows an NMR spectrum of fraction K in the region of aliphatic protons. Methyl protons directly attached to aromatic ring structure appear as singlets in the region of 2.2–2.7 ppm. In the case of mono-aromatic compounds, methyl protons generally appear at higher magnetic field than 2.3 ppm (14). In the case of two or more condensed aromatic ring structures, methyl protons appear at lower magnetic field than 2.4 ppm. Chemical shifts of some methyl protons attached to two and three condensed rings are listed in Table 3. The chemical shift values were determined from 600 MHz PMR spectra in CDCl_3 solution. Signals in the spectrum of fraction K which increased in their intensities by the small addition of these model compounds are marked in Fig. 7. Methyl protons of 1-methylnaphthalene appear at very low magnetic field of 2.66 ppm.

Methylene protons at β position to aromatic ring in partially hydrogenated polynuclear compounds appear in the region of 1.7-2.1 ppm. The multi-coupled signals centered at 1.77 ppm can be assigned as β -CH₂ protons in tetralin and its derivatives. Pentuplet signals at 2.05 ppm can also be assigned as β -CH₂ protons in indan and its derivatives. These conclusions were made by observing the decoupling effects on the multiplet structure of α -CH₂ protons after irradiating at the center of β -CH₂ proton signals in tetralin, indan and their alkyl derivatives. Fig. 8-(a) and (b) show the decoupled signals of α -CH₂ protons in tetralins and indans, respectively. The decoupled signals at 2.76 ppm in (a) and at 2.90 ppm in (b) correspond to α -CH₂ protons of unsubstituted tetralin and indan, respectively. The result of decoupling of Fig. 8 indicates the existence of several types of α -CH₂ protons in various derivatives of tetralin and indan. For example, the triplet at 3.10 ppm was also decoupled completely by the irradiation on the pentuplet signals at 2.05 ppm.

A methylene group resonance which joins two ring structures (bridgehead) appears at lower magnetic field, Table 3. The singlets at 3.36 and 3.88 ppm in fraction K can be assigned to acenaphthene and fluorene, respectively.

Figure 9 shows the aromatic proton signals of fraction K. Since more than half of aromatic protons of fraction K appear downfield from the benzene signal (7.37 ppm), this fraction contains a large amount of two and three condensed aromatic ring compounds. Two doublet signals (8.69 and 7.88 ppm) can be assigned to the protons of phenanthrene molecule at positions of 4,5 and 1,8, respectively (17). It is interesting to note that the content of anthracene in the fraction is negligible compared with phenanthrene in spite of the similar structures of three condensed-rings. The small signals in the

region of 8.47-8.63 ppm are also assigned to protons at the positions of 4 and 5 in methylphenanthrenes. This could be seen from 600 MHz ^1H spectra of 2- and 3-methylphenanthrene shown in Figure 10.

The assignment of ^1H signals of coal-liquid fractions in this study is based either on the comparison of chemical shift values of pure compounds or on the change of spectral intensities caused by the addition of such compounds. For example, 600 MHz NMR spectra of 2- and 3-methylphenanthrene are shown in Fig. 10. The assignment of each proton becomes much simpler by use of the higher-field spectrometer, because the chemical shift of each proton is extended compared with coupling constants, resulting in clear separation of each proton. The chemical shifts of the small signals in the region of 8.47-8.63 ppm in Fig. 9 correspond well to those in Fig. 10.

Figure 11 shows the aromatic proton signals of fraction K, C, D and G. Acidic fractions C and D, have more proton signals at higher magnetic field, because of the strong electron-donating property of phenolic OH groups. Acid-I(C) fraction contains condensed-ring aromatic compounds such as naphthols, while Acid-II(D) has no proton signal which appears downfield from the benzene signal. This shows that Acid-II is substantially composed of mono-aromatic phenols. The spectrum in the region of aliphatic protons in Acid-II is shown in Figure 12. The intense singlets in the region of 2.20-2.30 ppm are assigned to CH_3 protons attached to mono-aromatic ring. The acidic fractions are characteristic by having high content of such CH_3 groups. The results are consistent with substantial decrease of signals between 2.2-2.3 ppm after the removal of acidic fractions from fraction A, as shown in Fig. 2. Two triplets at 0.92 and 1.20 ppm may be assigned to CH_3 protons in ethyl and n-propyl groups

attached to aromatic rings, respectively. In conclusion, Acid-II fraction is mainly composed of alkyl substituted mono-aromatic phenols. It should be noted that the content of tetralinols is negligible though the existence of indanols can be identified in the spectrum. As for Base-II(G) fraction, proton signals are much more widely spread than that of fraction K particularly at lower magnetic field, as shown in Fig. 11. This may suggest that the fraction is composed of heteroaromatic compounds involving nitrogen atom in the ring structure (18).

Infrared spectra in dilute solution, Figure 3, indicate that compounds which contain acidic NH group such as indoles or carbazoles are substantially concentrated in Acid-I(C) fraction. Acid-I was further treated with cation-exchange resin to be separated into fractions H and I (Fig. 1). Solution infrared spectra of H and I, Figure 13, show that all phenolic species passed through the cation-exchange resin, whereas acidic nitrogen species were almost equally distributed into two fractions. It is interesting to note that NH species, possibly amides or amines whose stretching frequency appears at 3390 cm^{-1} (19), were substantially concentrated in fraction I. It is therefore concluded that fraction I (19% of Acid-I) contains negligible amount of phenolic compounds but two types of NH species and that it may be reactive with both anion and cation-exchange resins. Infrared spectra, Figures 3 and 13, were used for quantitative analysis of functional groups. The results are listed in Table 4. The contents of phenolic OH and acidic NH groups decrease in the following order:

Phenolic OH	$D > H > C > A \gg I, G, E \approx 0$
Acidic NH	$I > C > H \gg A > G > D, E \approx 0$

The absorbance ratio of C-H stretching of CH_3 -group to that of CH_2 group (20) increase in the following order:

$$A_{\text{CH}_3}/A_{\text{CH}_2} \quad \text{H, C, D} > \text{I} \approx 1.0 > \text{G} > \text{A} > \text{E}$$

The NMR structural parameter analysis of major fractions, Table 5, were calculated using a modified Brown and Ladner equations (5,6). The results indicate that Acid-II is largely composed of mono-aromatics, whereas Acid-I contains di-aromatics. Although Neutral and Base-II have almost the same molecular weights and aromaticity, the former is rich in condensed aromatic structure and the latter in saturated ring structure.

The NMR difference spectroscopic technique was used to examine major compositional changes among the SRC-II distillates obtained under the same process conditions but different feed coals. Elemental analysis, specific gravity and number average molecular weight of the three distillates are listed in Table 6. The data show no distinctive difference among them. Fig. 14(a) shows the difference spectrum between two SRC-II middle distillates derived from Illinois No. 6 and from Pittsburgh Seam. The proton signals above the center line represent the types of compounds present in Illinois No. 6 distillate in addition or in excess to compounds present in Pittsburgh Seam liquid. The product from Pittsburgh Seam Coal contains an excess amount of compounds whose resonance signals are displayed below the center line. The appearance of distinct resonance lines above the center line upfield to benzene and several intense singlets in the region of 2.20-2.30 ppm resemble the spectrum of Acid-II fraction. It may be that the product from Illinois No. 6 contains larger amount of alkyl substituted mono-aromatic phenols. On the other hand, product from Pittsburgh Seam contains larger amount of naphthalenes and tetralins.

The difference spectrum between products from Illinois No. 6 and Western Kentucky is shown in Fig. 14(b). In this case almost symmetrical signals can be found in both sides except for few signals. Slight changes in chemical shift of each signal may be brought about either by slight changes in structure of similar compounds in both coal-liquids, or by the presence of different compounds which affects the chemical shift of signals by intermolecular interaction. In conclusion, the chemical composition of these two coal-liquids is quite similar except for the fact that the product from Illinois No. 6 contains larger amount of saturate fraction or long chain substituents.

Conclusion

A coal-derived liquid (SRC-II) and its fractions are characterized by 600 MHz ^1H NMR spectrometer. Saturate fraction, being 8.1% by weight of unfractionated coal-liquid, is mainly composed of n-alkanes of high carbon numbers and the content of cycloalkanes is negligible. Aromatic fraction (49.0%) contains a considerable amount of partially hydrogenated polynuclear compounds. Double resonance techniques have been used for chemical shift identification of β -CH₂ and α -CH₂ protons attached to aromatic ring structures. The decoupled signals may be used for quantitative analysis of donor hydrogens, which are known to be effective in hydrogen-transfer phenomenon in coal-liquefaction processes. The aromatic fraction contains larger amounts of CH₃ group attached to condensed aromatic ring structures which appear as singlets in the region of 2.4-2.7 ppm, whereas in acidic fractions almost all benzylic CH₃ groups are attached to mono-aromatic ring structure (chemical-shift range of 2.2-2.3 ppm). The relatively strong acidic fraction, Acid-II (15.0%), can be recovered from anion-exchange resin by the elution with CO₂ saturated methanol after the

elution with benzene. Acid-II is substantially composed of alkyl substituted mono-aromatic phenols and 75% of the fraction boil in the narrow boiling-point range of 461-516 K (370-470 F).

The new NMR difference spectroscopic technique is applied to coal-derived liquids obtained from the same process conditions but from different coals. The slight compositional changes among the distillates are shown by the difference spectra. Such quick and direct characterization with minimal fractionation may help to assess the slight variation of process parameters in coal-liquefaction.

Acknowledgements

We acknowledge support of the U.S. Department of Energy to Duquesne University under Contract No. DE-AC22-80 PC 30252. The 600 MHz spectrometer at Carnegie-Mellon University, supported by PHS Grant No. RR-00292, was used, and we thank K. S. Lee and J. Dadok for expert advice in carrying out the NMR measurements.

Literature Cited

1. Friedel, R. A., J. Chem. Phys., 1959, 31, 280.
2. Brown, J. K., Ladner, W. R., and Sheppard, N., Fuel, 1959, 39, 79.
3. Brown, J. K. and Ladner, W. R., Fuel, 1959, 39, 87.
4. Schwager, I., Farmanian, P. A., and Yen, T. F., "Analytical Chemistry of Liquid Fuel Sources Tar Sands, Oil Shale, Coal, and Petroleum", p. 66-77, Advanced in Chemistry Series 170, Am. Chem. Soc., 1978.
5. Ouchi, K., Iwata, K., Makabe, M., and Itoh, H., Preprint, Div. Fuel Chem., Am. Chem. Soc., 1979, 24(1), 185.
6. Chung, K. E., Anderson, L. L., and Weiser, W. H., Preprint, Div. Fuel Chem., Am. Chem. Soc., 1979, 24(3), 243.
7. Bartle, K. D. and Jones, D. W., Fuel, 1969, 48, 21.
8. Schweighardt, F. K., Retcofsky, H. L., Friedman, S., and Hough, M., Anal. Chem., 1978, 50, 368.
9. Jewell, D. M., Weber, J. H., Bunger, J. W., Plancher, H., and Latham, D. R., Anal. Chem., 1972, 44, 1391.
10. Scheppele, S. E., Benson, P. A., Greenwood, G. J., Grindstaff, Q., Aczel, T., and Bieber, B., Preprint, Div. Petrol. Chem., Am. Chem. Soc., 1979, 24(4), 963.
11. Boduszynski, M. M., Preprint, Div. Petrol. Chem., Am. Chem. Soc., 1979, 24(4), 935.
12. Bothner-By, A. A. and Dadok, J., Paper presented at Symposium on "The Utility of 600 MHz NMR Spectroscopy in Biochemical and Organic Structure Determination", Pittsburgh, December 1979.
13. Tewari, K. C., Wang, J. T., Li, N. C., and Yeh, H. J. C., Fuel, 1979, 58, 371.

14. High Resolution NMR Spectra Catalog, Varian, Palo Alto, California, 1962.
15. Cannon, C. G. and Sutherland, G. B. B. M., Spectrochim. Acta 1951, 4, 373.
16. Selected NMR Spectral Data (100 MHz), Vol. I, Serial Numbers 51c, 69c, 89c, 98c, American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas A and M University, December 1972.
17. Jonathane, N., Gordon, S., and Dailey, B. P., J. Chem. Phys., 1962, 36, 2443.
18. Schafer, T. and Schneider, W. G., Can. J. Chem., 1963, 41, 966.
19. Schwager, I. and Yen, T. F., Anal. Chem., 1979, 51, 569.
20. Hathaway, C. D., Curtis, C. W., Meng, S., Tarrer, A. R., and Guin, J. A., Preprint, Div. Fuel Chem., Am. Chem. Soc., 1978, 23(1), 275.

Table 1. Elementary Analysis, Molecular Weights, Empirical Formulae of the Major Fractions of SRC II

Fraction		A	E	C	D	G
			Neutral	Acid-I	Acid-II	Base-II
Mol. Wt.*		161	180	156	128	182
Elementary Analysis:						
	C	86.09	89.96	80.57	77.32	81.50
	H	8.48	8.95	8.25	7.60	8.29
	O	3.99	0.61	8.91	14.66	1.39
	N	1.15	0.10	2.17	0.32	8.53
	S	0.29	0.38	0.10	<0.10	0.29
Empirical Formulae						
(No. of atoms per molecule)						
	C	11.6	13.5	10.5	8.2	12.4
	H	13.5	16.0	12.8	9.7	15.0
	O	0.40	0.07	0.87	1.17	0.16
	N	0.13	0.01	0.24	0.03	1.11
	S	0.01	0.02	0.00	0.00	0.02

* Number-average mol. wt., using VPO in CH_2Cl_2 solutions (3-8g/l) at 27°C.

Table 2. Percent Distribution of Heteroatoms

Fraction	E	C	D	G	Others
	Neutral	Acid-I	Acid-II	Base-II	
Yield (relative to A)	59.1%	11.1%	15.0%	6.6%	8.2%
% Distribution of Heteroatoms					
O:	9%	25%	55%	2%	9%
N:	5	21	4	49	21
S:	78-80	3-4	<3	7	9

Table 3. Chemical Shifts of CH₃ and CH₂ Protons in
Various Aromatic Compounds*CH₃ protons α to condensed aromatic rings:

(a) 1-methylnaphthalene	2.665 ppm
(b) 2-methylnaphthalene	2.492
(c) 2-methylphenanthrene	2.566
(d) 3-methylphenanthrene	2.632

Ring-joining CH₂ protons:

(e) fluorene	3.882
(f) acenaphthene	3.360
(g) 9,10-dihydrophenanthrene	2.862

*Determined in CDCl₃ solutions of about 20 g/l

Table 4. Quantitative Analysis of Functional Groups in Chromatographically Separated Fractions

Fraction	Absorbance or absorbance ratio ^a				
	^b A_{OH}	^c Relative A_{OH}	^d A_{NH}	^c Relative A_{NH}	^e A_{CH_3}/A_{CH_2}
A	0.197	1.0	0.061 ^f	1.0	0.82
C	0.309	1.6	0.100	5.8	1.14
H	0.515	2.6	0.096	5.5	1.14
I	0.015	0.08	0.125	7.2	1.00
D	0.815	4.1	0	0	1.11
E	0	0	0	0	0.75
G	0.009 ^g	0.00	0.117 ^g	0.91	0.91

a Measured in CCl_4 solutions, 1.09 g/l, 5 mm KBr liquid cell.

b Absorbance measured at 3600 cm^{-1} .

c Relative to absorbance of fraction A after normalization on concentration.

d Absorbance measured at 3480 cm^{-1} .

e Ratio of the absorbance at 2960 cm^{-1} (symmetrical stretching in CH_3 group) to the absorbance at 2925 cm^{-1} (symmetrical stretching in CH_2 group).

f CCl_4 solution of 3.84 g/l.

g CCl_4 solution of 8.05 g/l.

Table 5 Structural Parameters for Major Fractions of SRC II

Fractions		A	E Neutral	C Acid-I	D Acid-II	G Base II
Number of carbon atoms in a molecule	C'	11.55	13.49	10.47	8.25	12.36
	Ca'	7.51	7.99	6.74	6.21	7.14
	CαCH ₃	0.45	0.32	0.58	0.70	0.41
	CαCH ₂	1.46	1.65	1.37	0.73	2.32
	C'others	2.13	3.53	1.78	0.61	2.49
Structural parameters	f _a	0.65	0.59	0.64	0.75	0.58
	H _{au} /Ca'	0.90	0.78	0.93	1.00	0.94
	R _T	2.03	2.51	1.72	1.32	2.32
	R _A	1.38	1.63	1.20	1.03	1.26
	R _N	0.65	0.88	0.52	0.29	1.06

*a C' total carbon, Ca aromatic, CαCH₃ benzylic methyl, CαCH₂ benzylic methylene, C' other than Ca', CαCH₃ and CαCH₂.

*b f_a aromaticity, H_{au}/Ca' ratio of substitutable aromatic edge atoms to total aromatic atoms, number of total (R_T), aromatic (R_A) and naphthenic (R_N) rings in a molecule.

Table 6. Properties of SRC II Middle Distillates
from Different Coals

		Illinois #6	Pittseam	Western Kentucky
Elemental	C	85.55	86.03	85.37
Analysis	H	9.12	8.93	9.19
(wt%)	O	4.29	3.83	4.15
	N	0.85	1.04	1.09
	S	0.19	0.17	0.20
Specific				
Gravity		0.973	0.974	0.975
(289 K)				
Molecular				
Weight		172	185	186

Fig. 1. Scheme of Chromatographic Fractionation of SRC II

Fig. 2 600 MHz NMR spectra of fractions, A and B.
A n-Pentane-soluble oil of SRC II, B Acid-free fraction of A

CCl₄ solutions; 1.09 g/l (*3.84 g/l, ** 8.05 g/l)
 5mm KBr liquid cell

Fig. 3 Infrared spectra in carbon tetrachloride solutions.

Fig.4 Boiling Point Distribution for Fractions of SRC II

Fig. 5 Infrared spectra of various fractions of SRC 11: J, Saturates; K, Aromatic-1

Fig. 6 600 MHz NMR spectrum of Saturate fraction (J).

Fig. 7 600 MHz NMR spectrum of Aromatic-I fraction (K)
in the region of aliphatic protons.

Fig. 8-(a) Decoupling effect on α -CH₂ proton signals
in tetralin and its derivatives.

Irradiation at 1.773 ppm.

Fig. 8-(b) Decoupling effect of α -CH₂ protons
in indan and its derivatives.

Irradiation at 2.049 ppm.

Fig. 9 600 MHz NMR spectrum of Aromatic-I fraction (K)
in the region of aromatic protons.

28

Fig. 10 600 MHz NMR spectra of methylphenanthrenes.

Measured as CDCl_3 solutions of 10 g/l.

FIG. 11 600 MHz NMR spectra of fractions (K, C, D and G) in the region of aromatic protons.

Fig. 12 600 MHz NMR spectrum of Acid-II fraction (D) in the region
of aromatic protons.

D.

Fig. 13 Infrared spectra in carbon tetrachloride solutions.

Fig. 14-(a) Difference spectrum between SRC II Middle Distillate
from Illinois No.6 and from Pittsburgh Seam.

Measured as CDCl_3 solutions of 38.2 g/l.

Display, Illinois No.6 - Pittsburgh Seam

Fig. 14-(b) Difference spectrum between SRC II Middle Distillate
from Illinois No.6 and from Western Kentucky.

Measured as CDCl_3 solutions of 38.2 g/l.

Display, Illinois No.6 - Western Kentucky

Work in Progress on Aging of SRC Liquids

A 30-70 blend of SRC-I with SRC-II was subjected to oxygen aging at 62°C, and the viscosity increased dramatically after six days. The content of preasphaltene and its molecular size increase with time of aging, accompanied by decrease of asphaltene and pentane-soluble contents.

For the preasphaltene fraction on aging, gel permeation chromatography shows formation of large particles. ESR experiments show that with oxygen aging, spin concentration in the preasphaltene decreases. Perhaps some semiquinone, together with di- and tri-substituted phenoxy radicals, generated by oxygen aging of the coal liquid, interact with the free radicals already present in coal to yield larger particles and reduce free-radical concentrations. We are investigating the aging behavior of a blend composed of 20% SRC-I and 80% SRC-II (by weight) at room temperature and at 50°C, in the absence and presence of phenol, anisole, and o-phenylphenol as additives.

The pentane-soluble middle distillates of SRC-II from Pittsburgh seam and Illinois #6 coals contain a substantial amount of monophenols but are relatively stable to oxidative degradation. Metallic copper, however, accelerates the degradation as evident by an increase in viscosity and formation of pentane-insoluble components. Infrared spectra before and after aging with copper and oxygen show a significant reduction in the intensity of the free hydroxyl stretching vibration. Gel permeation chromatograms also show the formation of higher molecular size species upon aging. 600-MHz NMR spectra of the aged pentane-soluble fraction are similar to those of the unaged acid-free fraction. These results suggest that copper catalysis in the aging reaction of middle distillates involves the polymerization of acidic phenolic components.

For the aging of SRC liquids, we propose a mechanism for the oxidative coupling of phenols and work is in progress in the study of this mechanism.

PERSONNEL

The contract, DE-AC 22-80PC30252, is for the period August, 1980 to July, 1983. During the first quarter, August, 1980 to October, 1980, persons participating in the research are as follows: Dr. N.C. Li, 1/3 time; Dr. T. Hara (August only); Dr. L. Jones, full-time; Dr. N.F. Yaggi, (Sept. and Oct.). L.J.S. Young, J. Dru, and R. Diez have been students.