KINETICS AND MECHANISM OF CATALYTIC HYDROPROCESSING
OF COMPONENTS OF COAL-DERIVED LIQUIDS

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I. ABSTRACT

A new method of structural analysis is applied to a group of hydroliquefied coal samples. The method uses elemental analysis and NMR data to estimate the concentrations of functional groups in the samples. The samples include oil and asphaltene fractions obtained in a series of hydroliquefaction experiments, and a set of 9 fractions separated from a coal-derived oil. The structural characterization of these samples demonstrates that estimates of functional group concentrations can be used to provide detailed structural profiles of complex mixtures and to obtain limited information about reaction pathways.

II. OBJECTIVES
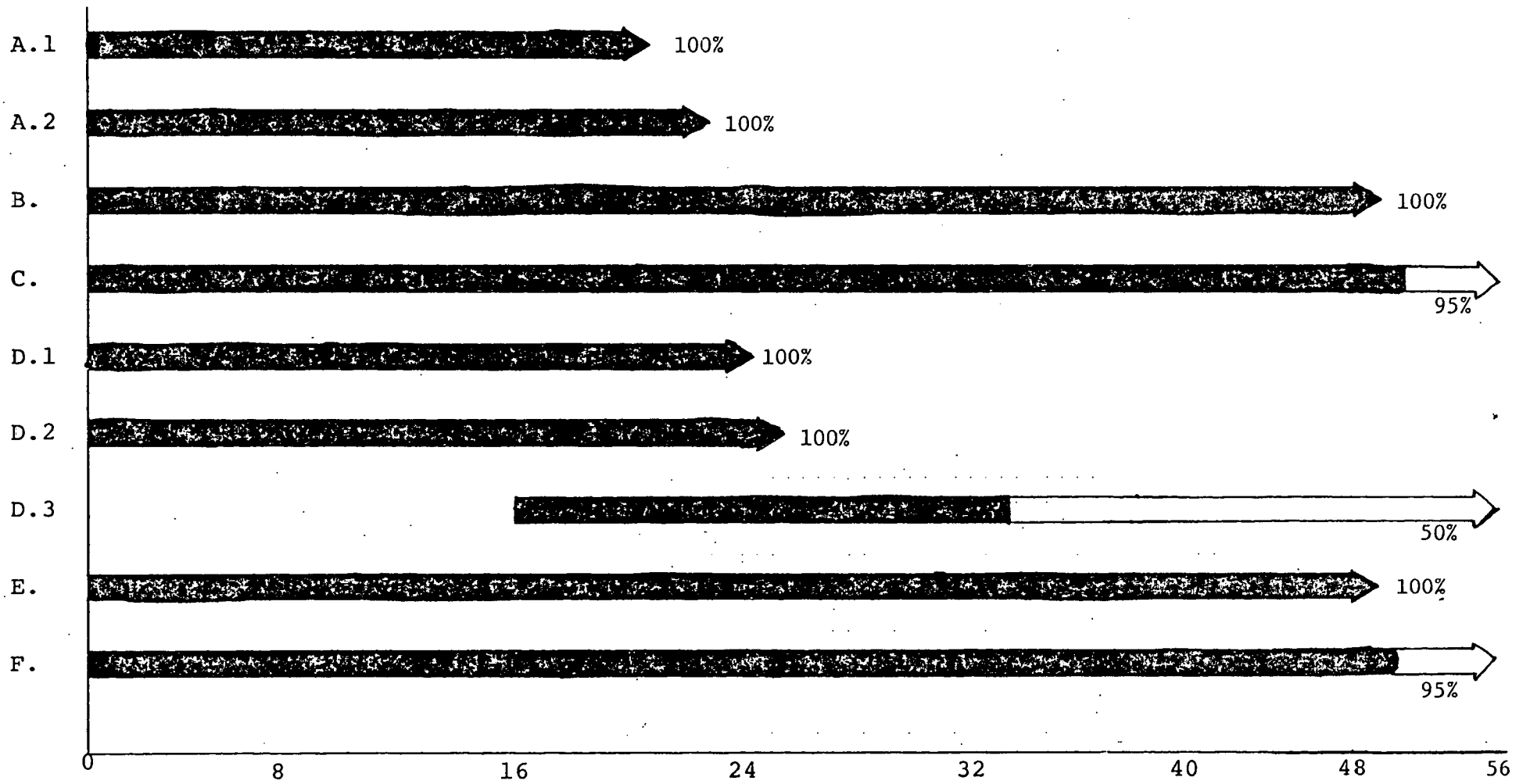
Statement of Work Outline

A.   Preparation of coal liquid fractions and pure compounds for hydroprocessing reaction studies

       1.   Fractions of coal-derived liquids separated by preparative chromatography

       2.   Detailed characterization of each fraction

B.   Conversion of coal-liquid fractions in high-pressure microreactors

       1.   Ni-Mo/Al_2O_3

       2.   Co-Mo/Al_3O_3

    *3.   Aged H-Coal catalysts

C.   Analysis of reaction products

       1.   Physical and chemical characterization

       2.   Determination of relative reactivities for hydrogenation, hydrocracking, and removal of heteroatoms

   **3.   Formulation of reaction networks

D.   Investigation of the role of hydrogen-donor molecules in catalytic hydrogenation and hydrodenitrogenation of synthetic coal-derived liquid fractions

       1.   Hydrogen-transfer reactants--biphenyl, quinoline, and acridine separately in hexadecane carrier oil

       2.   Three or more coreactants and inhibitors--quinoline, acridine, and carbazole in heterocyclic and aromatic solvents

       3.   Synthetic coal-derived liquids with all important components proportionately represented

E.   Characterization of aged H-Coal caalyst by electron microscopy, microprobe analysis, and other physical methods

F.   Representation of results in terms of engineering reaction networks and kinetics.

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*Insofar as time allows and samples can be obtained.
**As data warrant.

III. PROGRESS TO DATE: Work Schedule

A.1   100%

A.2   100%

B.   100%

C.   95%

D.1   100%

D.2   100%

D.3   50%

E.   100%

F.   95%

0   8   16   24   32   40   48   56

IV. CUMULATIVE EXPENDITURES BY QUARTER

QUARTER	PERSONNEL	TRAVEL	SUPPLIES & EXPENSES	GULF SUBCONTRACT	EQUIPMENT	MISCELLANEOUS*	OVERHEAD
First 5/15/79– 8/15/79	$ 14,101	$ ——	178	$ ——	$ ——	$ ——	$ 5,718
Second 8/15/79– 11/15/79	31,539	325	2,779	16,632	——	100	14,754
Third 11/15/79– 2/15/80	40,952	893	5,927	32,754	10	1,726	20,495
Fourth 2/15/80– 5/15/80	50,521	2,481	8,071	55,571	10	1,726	26,101
Fifth 5/15/80– 8/15/80	66,383	2,485	10,788	66,162	2,510	1,726	32,513
Sixth 8/15/80– 11/15/80	89,428	4,612	15,968	71,095	3,232	2,437	44,938
Seventh 11/15/80– 2/15/81	110,060	4,823	17,378	77,966	3,233	2,437	53,839
Eighth 2/15/81 5/15/81	131,318	4,823	24,672	82,777	9,419	2,437	65,260
Ninth 5/15/81– 8/15/81	159,870	4,829	29,687	88,658	24,479	2,965	78,900
Tenth 8/15/81– 11/15/81	176,469	6,744	31,486	92,679	24,479	2,965	87,025
Eleventh 11/15/81– 2/15/82	185,110	7,378	35,437	108,616	23,519	4,140	92,786
Twelfth 2/15/82– 5/15/82	192,289	9,368	41,799	119,695	26,121	4,920	99,173

IV. CUMULATIVE EXPENDITURES BY QUARTER

Thirteenth 5/15/82– 8/15/82	200,575	10,480	48,510	125,900	26,121	6,815	106,512
Fourteenth 8/15/82– 11/15/82	210,071	10,837	49,947	131,900	26,121	6,815	109,632
Fifteenth 11/15/82– 2/15/83	227,770	12,022	54,234	132,000	26,121	7,237	115,836
Sixteenth 2/15/83– 5/15/83	226,911	12,179	58,855	132,000	26,121	7,848	119,493
BUDGET	217,102	15,000	88,000	132,000	30,000	42,808	143,128

*Maintenance, Info. Processing

TOTAL BUDGET: $660,945   TOTAL EXPENDED TO DATE: $583,307

V. EXPERIMENTAL WORK, RESULTS AND DISCUSSION

INTRODUCTION

Characterizing the structures of fuels derived from coal is an important step in developing an understanding of the chemistry of coal reactions. The determination of exact chemical structures of coal liquids from elemental composition, Nuclear Magnetic Resonance (NMR) and possibly other analytical data is an underdetermined problem, however, because of the complexity and variety of the molecules in the liquids. Since the molecular structures cannot be fully delineated, recourse must be made to approximate characterization methods. The data on which such characterizations are most commonly based are elemental analysis, ^{1}H nmr spectra, and less routinely, ^{13}C nmr spectra.

Structural characterization most frequently takes the form of a representative molecular structure, or a set of average parameters, such as carbon aromaticity, average length of alkyl chains, and the degree of aromatic substitution[1-5]. In this work, we apply an alternative method of structural characterization, termed functional group analysis. The goal of functional group analysis is to calculate the concentrations of the functional groups present in the sample. The method is based on the premise that although the number of individual molecular species in a coal liquid is large, most of these species are composed of a limited number of functional groups. The relative concentrations of the functional groups determine the chemical behavior of the liquids. Thus, calculating the concentrations of the major functional groups is a useful structural characterization.

A set of functional groups appropriate for the characterization of hydrotreated coal liquids is given in Figure 1. This set is not a complete listing of all structures known to be present in coal liquids. Rather, it is a concise representation of the major structural features of hydrotreated coal liquids, i.e., aromatic clusters, hydroaromatic groups, alkyl chains, bridges and heteroatomic groups. The method of functional group analysis seeks to calculate the concentrations of these groups utilizing elemental composition, NMR, and possibly other supplemental data. An extensive description of the methodology has been given[6]. Briefly, the NMR and elemental analysis data are used to construct linear balance equations. In these balance equations, the concentration of each atomic species is expressed as a sum of the contribution from the functional groups, each with a suitable stoichiometric coefficient. For example, the concentration of aromatic carbon equals 6 times the concentration of monoaromatic groups plus ten times the concentration of diaromatic groups plus.... . The set of balance equations can be written succinctly in the matrix form

$$\sum_{j=1}^{n} A_{ij} y_j = b_i \quad (i = 1,...m) \tag{1}$$

where y_j (j=1,...n) are the unknown functional group concentrations, b_i (i=1,...m) are atomic species concentrations and A_{ij} are stoichiometric coefficients. The number of equations is smaller than the number of unknowns, m<n.

In addition to the constraints imposed by the balance equations, there are the constraints of non-negative concentrations

$$y_j \geq 0 \qquad\qquad (2)$$

Equations 1 and 2 define a space of feasible solutions. The structure of the coal liquid is characterized by selecting a single solution from the feasible space. To select a solution, we adopt a procedure that is computationally straightforward. The set of concentrations $y_i \ldots y_n$ is selected such that a function $P(y_i \ldots y_n)$ is minimized. The form of the function depends on what, if any, data are available in addition to elemental analyis and NMR. For example, if no data are available other than the constraints of equations 1 and 2, equation 3 is minimized.

$$P = \sum_{i=1}^{m} \sum_{j=1}^{n} (\frac{b_i}{A_{ij} N_i} - y_j)^2 \qquad\qquad (3)$$

where N_i is the number of functional groups containing species i. Equation 3 was constructed by assuming that the distribution of atomic species among he functional groups was random[6]. Concentrations obtained by minimizing this equation subject to the constraints of equations 1 and 2 were found to be in good agreement with functional group concentrations based on high resolution mass spectral data and with the results of other methods of structural analysis[6]. The function to be minimized can be modified to incorporate qualitative information based on data other than NMR and elemental analysis.

For example, the function to be minimized if high resolution mass spectra are available is equation 4.

$$P = \sum_{i=1}^{n} (y_i - f_i)^2 \qquad (4)$$

where f_i is the concentration of functional group i predicted by the mass spec data[6].

In this work, functional group concentrations will be estimated for two sets of synthetic fuel samples utilizing elemental analysis, ^{1}H NMR and ^{13}C NMR data. The first set of samples is a group of 10 fractions of a solvent refined coal. Analysis of these samples will demonstrate how the functional group method can be used to provide detailed descriptions of complex mixtures. The second set of samples is a group of asphaltene and oil fractions obtained in a series of coal hydroliquefaction experiments. The functional group concentrations obtained for these samples will help to identify liquefaction pathways.

EXPERIMENTAL

In an extensive series of experiments, Powhatan #5 coal was hydroprooessed under a variety of conditions. Experimental procedures are given below and the coal liquids obtained are listed in Table 1.

Solvent Refined Coal Fractions

A heavy distillate obtained from a 50 ton/day SRC-II demonstration plant operating with Powhatan #5 coal was fractionated using a SARA chromatographic procedure[7]. The goal of the separation was to isolate heteroatomic functionalities. The ten primary fractions obtained were neutral oils (72.5 wt%), asphaltenes (8.9%), very weak bases (2.7%), weak bases (1.9%), strong bases (6.0%), very weak acids (1.1%), weak acids (1.2%), strong acids (0.2%), neutral resins (1.2%) and saturates (4.5%). Elemental composition, ^1H NMR and ^{13}C NMR data were obtained for the fractions. The data are given in Table 2.

Hydroliquefied Coal Samples

A group of pentane soluble and toluene soluble/pentane insoluble extracts were obtained from the products of a series of autoclave experiments. The samples were prepared by shaking a reactor containing 5 g of a Powhatan #5 coal and 5 g of a liquefaction solvent in a heated fluidized sand bath. The reactor consisted of a 22 ml stainless steel bomb with a .64 cm (1/4-in.) stainless steel gas inlet tube. In each run, the reactor was pressurized to 11.0 MPa (109 atm) with hydrogen and was shaken in the sand bath for the specified time. Not included in the nominal reaction time was the reactor heating time, i.e. the time required for the reactor's internal temperature to reach within 1°C of the sand bath temperature. Heating time was found to be 4 minutes at both 400 and 460°C.

After the necessary time had elapsed, the reactor was removed from the sand bath and cooled with an air jet. About 2 minutes were required to cool the sample to 300°C. After 7 to 10 minutes of cooling, the reactor was immersed in crushed dry ice. The reaction products were removed from the

reactor with a methylene chloride wash. The methylene chloride was then driven off at room temperature by a nitrogen purge. Pentane and toluene extracts were obtained by successive Soxhlet extractions. The pentane and toluene were driven off, along with the liquefaction solvent, by heating the extracts at 60°C under a nitrogen stream.

The reaction conditions were varied to determine the effect of solvent, temperature and residence time on product structure. Tetralin and the SRC-II heavy distillate (SHD) described above were chosen as solvents to represent different hydrogen donating capabilities. Experiments were done at two temperatures and three residence times.

Proton NMR, ^{13}C NMR and elemental analysis data were obtained for each of the samples. The results of the elemental analysis and the yields of the extractions are listed in Table 3. The NMR data are given in Table 4. Sharp peaks at 6.8 and 2.2 ppm were noted in the ^{1}H spectra of some of the toluene extracts. The peaks were believed to be the result of residual toluene from the extractions, and were subtracted from the spectra. In all cases, the toluene present represented less than 9% of the sample.

RESULTS AND DISCUSSION

For each liquid sample, the concentrations of the functional groups listed in Figure 1 were calculated. In some cases, functional groups were assigned concentrations of zero. For example, when separation procedures were specifically designed to exclude certain functionalities, e.g., phenolics in the neutral oil fraction of the SRC heavy distillate, the concentrations of

those functionalities were set equal to zero. IR spectra were particularly
helpful in determining the presence or absence of some functional groups in
the samples.

The results of the functional group analysis for both sets of samples
are discussed below. For the hydroliquefied samples, the functional group
concentrations were obtained by minimizing equation 3 subject to the
constraints of equations 1 and 2. The concentrations obtained for the SRC
fractions were selected by minimizing a function which utilizes qualitative
data based on ^1H NMR spectra[8]. Use of two different methods of selecting a
particular solution from the feasible space emphasizes the versatility of the
functional group analysis algorithm in handling new sources of data.

Solvent Refined Coal Fractions

The samples examined here are the fractions obtained from a SRC-II
heavy distillate was separated into ten fractions which differ primarily in
the heteroatomic functionalities which they contain. IR and NMR spectra were
used to identify the functional groups present in each fraction[9,10].

Functional group analysis was applied to each of the ten fractions and
the resulting concentrations are given in Table 5. The concentrations were
obtained by selecting the solution which had a distribution of aromatic ring
sizes closest to that predicted by the method of Tominaga[8]. The
distribution of ring sizes could have been included in the constraints of
equation 1, however these data are more qualitative than the constraints of
equation 1 and are therefore more appropriately used in the selection of a
solution from the feasible space rather than in defining the feasible space.

Thus, a solution was selected from the feasible space by minimizing equation 5 subject to the constraints of equations 1 and 2.

$$P = (C_i - 2y_2 - 4y_3 - 6y_4)^2 \tag{5}$$

where C_i is the concentration of internal carbon in the sample[8].

Examination of the functional group concentrations reveals that the neutral oils and the asphaltenes have a higher hydroaromatic content than the various acids and bases. High concentrations of aliphatic chains and small aromatic rings appear to be associated with high heteroatomic concentrations. Another interesting feature of the results is the ring size distribution. The neutral oils are predicted to contain mostly diaromatic rings, while the remainder of the fractions are predominantly monoaromatic. The causes and significance of this result are not yet clear.

The functional group concentrations of the whole heavy distillate were determined from the concentrations and yields of each of the fractions. The 22 concentrations, which are given in Table 5, provide a detailed structural profile of the heavy distillate and provide a reasonable starting point for the kinetic modelling of this coal liquid.

Hydroliquefied Samples

The pentane and toluene extracts examined here contain liquefaction products of moderate molecular weight. Low molecular weight products (carbon number < 10) are removed with the liquefaction solvent and very high molecular weight products tend to be insoluble in pentane and toluene. The purpose of

the hydroliquefaction experiments was to help define the structures and obtain clues about the reaction pathways of these moderate molecular weight products.

We start by examining the data of Tables 3 and 4. The samples liquefied in tetralin and SRC-II heavy distillate (SHD) exhibit some straightforward trends. As the residence time increases, aromatic carbon increases, aliphatic carbon and hydrogen decrease. The samples are also deoxygenated. The changes in the content of aliphatic carbon and various types of aliphatic hydrogen are more pronounced in the samples generated in the solvent SHD relative to the samples generated in tetralin. They are also more pronounced in the toluene fractions compared to the pentane fractions.

The functional group concentrations of Tables 6 and 7 suggest the following interpretation of these data. Partially hydrogenated aromatic structures are partially or completely dehydrogenated and the hydroaromatic portion of some of these structures is being cleaved. Multiple ring hydroaromatic groups (functional groups 12 and 13) appear to be more labile than single ring hydroaromtics (group 8). An indication of the relative rates of the different modes of hydroaromatic group decomposition is given by calculating the percentage of hydroaromatic carbons that are converted to alkyl and aromatic carbon. Alkyl groups will result from splitting of hydroaromtics; aromatic groups will result from dehydrogenation. Comparison of samples 460T03 and 460T40 shows a decrease in hydroaromatics (groups 8, 12 and 13) amounting to 1.63 moles of carbon per 100 g of sample. Alkyl carbon increases by .44 moles/100 g and aromatic carbon increases 1.05 moles/100 g, so dehydrogenation reactions appear to dominate in tetralin at 460°C. In the pentane soluble fractions generated in tetralin and in both SHD fractions,

alkyl chains decrease and aromatic rings increase in concentration with reaction time. For these fractions, dehydrogenation is also the dominant mode of hydroaromatic decomposition.

As the hydroaromatic groups dehydrogenate, the hydrogen donating ability of the fractions decreases. This decrease is less pronounced when liquefaction solvents with good hydrogen donor properties are used. This observation indicates that the oils and asphaltenes can both accept hydrogen from the liquefaction solvent and donate hydrogen to other product fractions. The donation reactions appear to be more extensive than the hydrogen accepting reactions, as evidenced by the overall loss of hydrogen in the fractions with increasing reaction time.

CONCLUSIONS

Application of the proposed method of functional group analysis to two sets of coal-derived liquids has provided the following conclusions. The method can be applied in conjunction with separation procedures to provide detailed profiles of complex, multi-component mixtures. The method can also be used to obtain qualitative information about reaction pathways.

In general, functional group analysis is best suited for the structural analysis of complex liquids on which a large amount of data from a variety of sources is available. When applied, the method has several distinct advantages over other methods of structural characterization. It allows data from diverse sources such as NMR, IR and separation procedures to be incorporated into a single characterization; changes in structure are easily quantified; the types of structures present are easily visualized and

the results could provide a starting point for kinetic modeling.

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ACKNOWLEDGEMENT

VI. Publications Resulting from this DOE Project

1.   "Hydrodesulfurization of Benzo[b]naphthol[2,3-d]thiophene Catalyzed by Sulfided $CoO-MoO_3/\gamma-Al_2O_3$: The Reaction Network," A. V. Sapre, D. H. Broderick, D. Fraenkel, B. C. Gates, and N. K. Nag, *AIChE Journal* 26, 690 (1980).

2.   "Hydrogenation of Aromatic Hydrocarbons Catalyzed by Sulfided $CoO-MoO_3/\gamma-Al_2O_3$: Reactivities and Reaction Networks," A. V. Sapre and B. C. Gates, *Ind. Eng. Chem. Proc. Des. Dev.* 20, 68 (1981).

3.   "Hydrogenolysis and Hydrogenation of Dibenzothiophene Catalyzed by Sulfided $CoO-MoO_3/\gamma-Al_2O_3$: The Reaction Kinetics," D. H. Broderick and B. C. Gates, *AIChE Journal* 27, 663 (1981).

4.   "Catalytic Upgrading of Coal Liquids: Preparation and Characterization of Microreactor Feeds," L. Petrakis, R. G. Ruberto, D. C. Young, S. Katti, D. W. B. Westerman, and B. C. Gates, Proceedings, International Conference on Coal Science, Düsseldorf, p. 516 (1981).

5.   "Hydrogenation of Biphenyl Catalyzed by Sulfided $CoO-MoO_3/\gamma-Al_2O_3$: The Reaction Kinetics," A. V. Sapre and B. C. Gates, *Ind. Eng. Chem. Proc. Des. Dev.* 21, 86 (1982).

6.   "Hydrogenation of Aromatic Compounds Catalyzed by Sulfided $CoO-MoO_3/\gamma-Al_2O_3$," D. H. Broderick, A. V. Sapre, B. C. Gates, H. Kwart, and G. C. A. Schuit, *J. Catal.* 73, 45 (1982).

7.   "Hydroprocessing of Phenothiozine Catalyzed by $Co-Mo/\gamma-Al_2O_3$," H. Kwart, J. Katzer, and J. Horgan, *J. Phys. Chem.* 86, 2641 (1982).

8.   "Catalytic Hydroprocessing of SRC-II Heavy Distillate Fractions. I. Preparation of the Fractions by Liquid Chromatograph," L. Petrakis, R. G. Ruberto, D. C. Young, and B. C. Gates, *Ind. Eng. Chem. Proc. Des. Dev.*, 1983, 22, 292.

9.   "Catalytic Hydroprocessing of SRC-II Heavy Distillate Fractions. II. Detailed Structural Characterization of the Fractions," L. Petrakis, D. C. Young, R. G. Ruberto, and B. C. Gates, *Ind. Eng. Chem. Proc. Des. Dev.*, 1983, 22, 298.

10.   "Hydrodeoxygenation of 1-Naphthol: Activities and Stabilities of Molybdena and Related Catalysts," M. W. Vogelzang, C.-L. Li, G. C. A. Schuit, B. C. Gates, and L. Petrakis, *J. Catal.*, submitted.

11.   "Capillary Column Gas Chromatography with Sulfur- and Nitrogen-Specific Hall Detectors for Determination of Kinetics of Hydroprocessing Reactions of Individual Compounds in Coal-Liquid Fractions," D. W. B. Westerman, S. S. Katti, M. W. Vogelzang, C.-L. Li, B. C. Gates, and L. Petrakis, *Fuel*, submitted.

12.   "Functional Group Analysis of Synthetic Fuels," D. Allen, L. Petrakis, G. R. Gavalas, and B. C. Gates, *Anal. Chem.*, submitted.

13. "Hydroprocessing of Organo-Oxygen Compounds in Coal Liquids Catalyzed by Sulfided Ni-Mo/γ-Al₂O₃," C.-L. Li, S. S. Katti, B. C. Gates, and L. Petrakis, _J. Catal._, submitted.

14. "Determination of Oxygen Functionalities in Synthetic Fuels by NMR of Naturally Abundant ^{17}O," D. W. Grandy, L. Petrakis, D. C. Young, and B. C. Gates, _Science_, submitted.

15. "Kinetics of Acridine Hydrodenitrogenation," R. Zawadzki, S. S. Shih, E. Reiff, J. R. Katzer, and H. Kwart, to be submitted.

16. "Quinoline Hydrodenitrogenation: Reaction Networks and Kinetics," S. S. Shih, K. N. Mathur, J. R. Katzer, H. Kwart, and A. B. Stiles, to be submitted.

17. "Reactivity of Selected Six-Ring Nitrogen-Containing Compounds in Hydrodenitrogenation," K. N. Mathur, Z. Sarbak, N. Islam, H. Kwart, and J. R. Katzer, to be submitted.

18. "Catalytic Hydroprocessing of SRC-II Heavy Distillate Fractions. 3. Hydrodesulfurization of the Neutral Oils," S. S. Katti, D. W. B. Westerman, B. C. Gates, T. Youngless, and L. Petrakis, _Ind. Eng. Chem. Proc. Des. Dev._, submitted.

19. "Catalytic Hydroprocessing of SRC-II Heavy Distillate Fractions. 4. Hydrodeoxygenation of Phenolic Compounds in the Acidic Fractions," C.-L. Li, Z.-R. Xu, B. C. Gates, and L. Petrakis, _Ind. Eng. Chem. Proc. Des. Dev._, submitted.

20. "Hydrodeoxygenation of 1-Naphthol Catalyzed by Sulfided Ni-Mo/γ-Al₂O₃: The Reaction Network," C.-L. Li, Z.-R. Xu, Z.-A. Cao, B. C. Gates, and L. Petrakis, _AIChE J._, submitted.

VII. PERSONNEL

Besides the principal investigators, the research team at the University of Delaware includes Ph.D. students Sanjeev Katti and Michael Girgis. Both Scott Starry and Souran Banerjee continue their work as undergraduate assistants.

Table 1

Coal Liquid Samples

I Fractionated SRC-II Heavy Distillate

    Fractions

        Neutral oils
        Asphaltenes
        Very weak bases
        Weak bases
        Strong bases
        Very weak acids
        Weak acids
        Strong acids
        Neutral resins

II Hydroliquefied coal fractions-pentane soluble and toluene soluble/
    pentane insoluble fractions obtained for each experiment

Experimental Conditions

Sample No.	Solvent	Reaction Temperature	Reaction Time (min)
400T40	Tetralin	400°C	40
460T03	Tetralin	460°C	3
460T10	Tetralin	460°C	10
460T40	Tetralin	460°C	40
400S40	SRC-II heavy distillate	400°C	40
460S03	SRC-II heavy distillate	460°C	3
460S10	SRC-II heavy distillate	460°C	10
460S40	SRC-II heavy distillate	460°C	40

Table 2

Elemental Analysis and NMR Data for SRC-II Heavy Distillate Fractions

Fraction	Yield (wt% of Heavy Distillate)	Elemental Analysis Data %C	%H	%N	%O	%S	NMR Data %Aromatic	^{1}H NMR* %Alpha	%Beta	%Gamma	Carbon Aromaticity
Neutral oils	76.86	91.4	7.2	0	.72	.66					
Aromatic fraction of neutral oils	72.49						49	28	17	6	.77
Asphaltenes	8.88	85.4	6.4	3.2	4.5	.47	59	28	10	3	.81
Very weak bases	2.69	84.3	6.8	1.3	7.1	.52	56	25	14	5	.81
Weak bases	1.87	78.8	6.7	3.9	8.3	2.2	44	23	23	10	.74
Strong bases	5.99	85.9	6.8	4.8	1.8	0.60	44	31	19	7	.74
Very weak acids	1.08	82.2	8.0	.21	8.9	.16	48	32	16	4	.74
Weak acids	1.24	82.3	7.7	0	9.8	.16	58	25	11	4	.79
Strong acids	.21	76.0	5.6	0	17.8	.60	53	32	11	3	.79
Neutral resins	1.19	84.6	7.2	.85	7.2	.15	29	20	35	16	.67
Saturates	4.52						0	0	74	26	.00

*Chemical shift assignments from Snape et al. [1].

Table 3

Extraction Yields and Elemental Analysis Data for Hydroliquefied Samples

	Pentane Fraction				Toluene Fraction			
Sample	Yield[*]	%C	%H	%O	Yield[**]	%C	%H	%O
400S40	.117	89.5	7.4	2.2	.197	84.1	6.3	5.3
460S03	.106	88.2	7.2	2.4	.136	84.6	5.7	6.5
460S10	.154	89.0	7.0	2.2	.141	86.0	5.3	5.5
460S40	.103	90.3	6.6	2.0	.101	88.2	5.0	4.4
400T40								
460T03	.322	82.2	7.4	5.4	.176	83.9	6.4	6.4
460T10	.423	85.0	7.2	4.5	.183	86.0	6.2	6.0
460T40	.491	87.8	7.0	3.6	.213	87.9	6.0	5.4

$$* \quad \text{Pentane Yield} = 1 - \frac{\text{Wt Pentane Insolubles}}{\text{Wt Ash-Free Coal}}$$

$$** \quad \text{Toluene Yield} = 1 - \frac{\text{Wt Toluene Insolubles}}{\text{Wt Ash-Free Coal}} - \text{Pentane Yield}$$

Table 4

^{1}H NMR and ^{13}C Data for Pentane Fractions

Sample[†]	Aromatic H (9.0-5.0ppm)[*]	αH (5.0-1.9 ppm)[*]	βH (1.9-1.0 ppm)[*]	γH (1.0-.5 ppm)[*]	Carbon Aromaticity
400S40	45.6	25.9	21.2	7.2	.74
460S03	44.6	28.6	20.1	6.6	.72
460S10	48.4	29.5	17.3	4.8	.76
460S40	56.3	31.5	10.2	1.9	.81
400T40	23.1	38.1	29.5	9.3	.51
460T03	28.4	34.3	27.8	9.5	.54
460T10	29.4	33.9	28.3	8.5	.60
460T40	30.0	36.3	25.7	8.0	.69

^{1}H NMR and ^{13}C Data for Toluene Fractions

Sample	Aromatic H	αH	βH	γH	Carbon Aromaticity
400S40	39.8	33.6	21.4	5.2	.79
460S03	48.7	32.4	14.9	4.1	.82
460S10	52.4	32.3	11.9	3.5	.84
460S40	66.7	24.2	7.5	1.7	.90
400T40	32.8	36.0	24.9	6.4	.67
460T03	33.9	38.0	23.7	4.4	.70
460T10	43.5	36.2	16.4	3.9	.75
460T40	53.6	29.7	13.3	3.4	.80

* Chemical shift assignments from Snape et al. [11].

† The sample number consists of the reaction temperature, solvent and reaction time, consecutively.

Table 5

SRC-II Heavy Distillate Functional Group Concentrations
(Concentrations in Moles/100g)
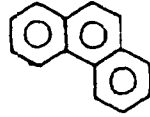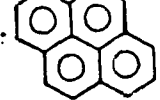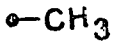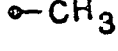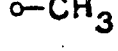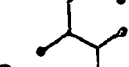
Functional Group	Neutral Oils (Aromatics)	Asphaltenes	Fraction Very Weak Bases	Weak Bases	Strong Bases	Very Weak Acids	Weak Acids	Strong Acids	Neutral Resins	Saturates	Whole Heavy Distillate
1. ⬡ (benzene)	.035	.874	.249	.320	.301	.796	.788	.139	.150	–	.154
2. ⬡⬡ (naphthalene)	.364	.006	.104	.003	.089	.002	.016	.045	.001	–	.273
3. ⬡⬡⬡ (phenanthrene)	.080	.014	.188	.079	.072	.008	.016	.209	.192	–	.073
4. ⬡⬡⬡⬡ (pyrene)	.042	.005	.021	.009	.052	.006	.015	.020	.054	–	.036
5. ◦—CH$_3$	.073	.005	.339	.480	.218	.555	.671	.604	.680	–	.108
6. ◦—CH$_3$	.054	.001	.001	.266	.001	.159	.199	.117	.801	–	.058
7. ◦—CH$_3$	.136	.064	.113	.223	.160	.106	.103	.057	.383	–	.128
8. ⬡ (cyclohexane)	.142	.001	.001	.035	.001	.055	.001	.001	.001	–	.104
9. (branched chain)	.063	.001	.001	.001	.001	.099	.001	.001	.001	–	.047
10. (branched chain)	.190	.143	.050	.001	.048	.076	.001	.001	.001	–	.155
11. (chain)	.018	.001	.001	.001	.001	.029	.001	.001	.001	–	.014
12. (decalin)	.041	.007	.096	.075	.093	.052	.031	.029	.045	–	.041
13. (decalin)	.025	.157	.002	.001	.107	.012	.002	.001	.001	–	.039

Table 5 (cont.)

(Concentrations in Moles/100 g)

Functional Group	Neutral Oils (Aromatics)	Asphaltenes	Very Weak Bases	Weak Bases	Strong Bases	Very Weak Acids	Weak Acids	Strong Acids	Neutral Resins	Saturates	Whole Heavy Distillate
14. ~O~	.048	–	–	–	–	–	–	–	–	–	.035
15. —OH	–	.281	.443	.519	.112	.556	.204	–	–	–	.062
16. —C(=O)—OH	–	–	–	–	–	–	.204	.555	.150	–	.005
17. (dibenzothiophene, S)	.020	.015	.016	.069	.019	.005	.005	.019	.005	–	.019
18. (pyridine, N)	–	–	–	.279	.172	–	–	–	–	–	.016
19. —NH$_2$	–	–	.093	–	.172	–	–	–	–	–	.013
20. (carbazole, N–H)	–	.230	–	–	–	.015	–	–	.061	–	.021
21. —C(=O)—	–	–	–	–	–	–	–	–	.150	–	.002
22. CH$_2$ in saturated structures	–	–	–	–	–	–	–	–	–	7.14	.309

Table 6

Pentane Soluble Fraction of Hydroliquefied Samples
(Concentrations in Moles/100g)
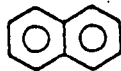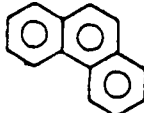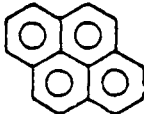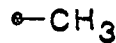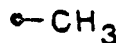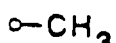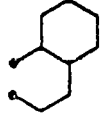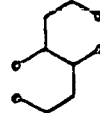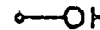
Functional Group	Liquefied in Tetralin				Liquefied in SHD			
	400° 40 min	460° 3 min	460° 10 min	460° 40 min	400° 40 min	460° 3 min	460° 10 min	460° 40 min
(benzene ring)	.343	.320	.188	.188	.235	.270	.230	.247
(naphthalene)	.096	.102	.112	.126	.142	.139	.141	.156
(phenanthrene)	.040	.052	.079	.093	.099	.088	.100	.112
(pyrene)	.002	.014	.067	.085	.083	.066	.086	.099
$-CH_3$	.413	.283	.263	.427	.356	.302	.315	.323
$-CH_3$	.102	.062	.245	.406	.300	.140	.150	.074
$-CH_3$	.229	.234	.204	.187	.177	.158	.112	.042
(cyclohexane)	.199	.162	.148	.157	.144	.132	.114	.092
(CH2 chain)	.001	.000	.023	.204	.000	.000	.015	.075
(CH2 chain)	.074	.062	.137	.105	.083	.106	.124	.125
(ether)	.000	.000	.000	.159	.000	.000	.000	.000
(decalin)	.158	.149	.074	.000	.020	.063	.028	.002
(hydroaromatic)	.044	.069	.081	.035	.031	.040	.048	.033
$-OH$	.338	.338	.281	.225	.138	.150	.138	.125

Table 7

Toluene Soluble Fraction of Hydroliquefied Samples
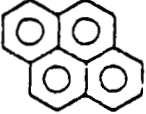### (Concentrations in Moles/100g)
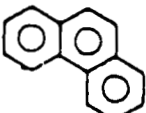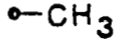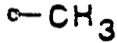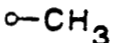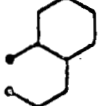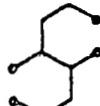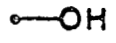
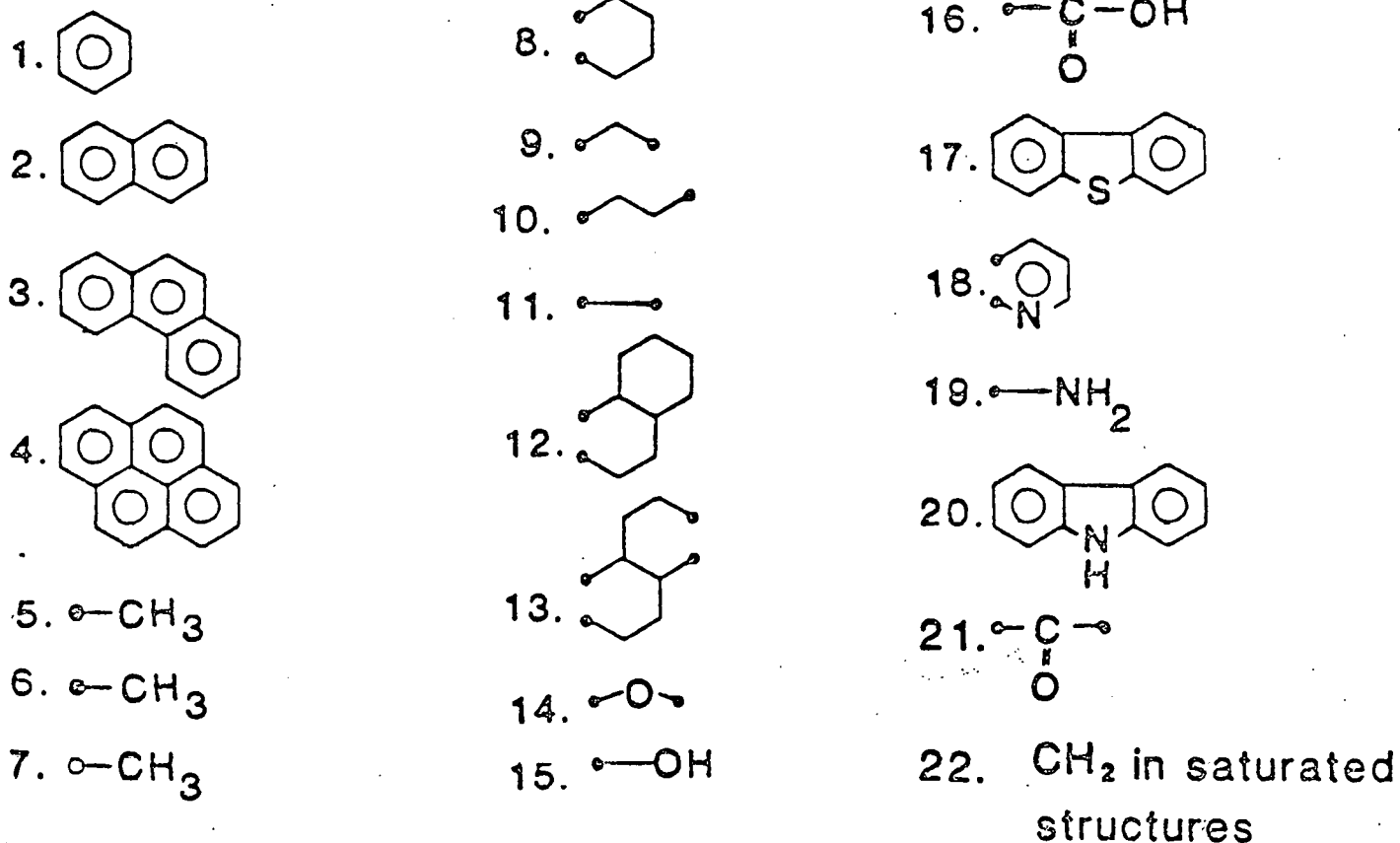| Functional Group	Liquefied in Tetralin				Liquefied in SHD			
	400° 40 min	460° 3 min	460° 10 min	460° 40 min	400° 40 min	460° 3 min	460° 10 min	460° 40 min
(benzene ring)	.176	.182	.200	.218	.151	.215	.223	.246
(naphthalene)	.114	.122	.134	.146	.116	.144	.150	.165
(phenanthrene)	.083	.091	.100	.109	.145	.108	.111	.123
(pyrene)	.075	.083	.091	.099	.090	.098	.102	.112
●—CH₃	.129	.276	.195	.128	.856	.410	.247	.212
●—CH₃	.123	.235	.095	.051	.478	.199	.111	.072
●—CH₃	.136	.094	.081	.068	.109	.078	.062	.028
(cyclohexyl)	.101	.119	.083	.061	.006	.082	.069	.044
(chain)	.182	.237	.244	.201	.001	.128	.171	.116
(chain)	.133	.118	.123	.099	.001	.059	.084	.056
(—)	.000	.063	.046	.105	.406	.384	.453	.568
(decalin)	.077	.026	.032	.033	.000	.000	.000	.000
(decalin)	.084	.056	.057	.050	.000	.000	.021	.002
●—OH	.400	.400	.375	.338	.331	.406	.344	.275

FIGURE CAPTIONS

Number	Title
1	Coal Liquid Functional Groups

Figure 1

Coal liquid functional groups

1. ⬡

2. ⬡⬡

3. (three fused rings)

4. (four fused rings)

5. ○—CH₃ → $\circ{-}CH_3$

6. ○—CH₃ → $\bullet{-}CH_3$

7. ○—CH₃ → $\circ{-}CH_3$

8. (saturated ring)

9. (chain)

10. (chain)

11. ○—○

12. (fused ring structure)

13. (fused ring structure)

14. ○—O—○

15. ●—OH

16. ○—$\overset{\displaystyle}{\underset{O}{C}}$—OH

17. (dibenzothiophene, S)

18. (pyridine, N)

19. ●—NH₂ → $\bullet{-}NH_2$

20. (carbazole, NH)

21. ○—$\overset{\displaystyle}{\underset{O}{C}}$—○

22. CH₂ in saturated structures

Notation:

○— bound directly to an aromatic ring

●— bound to a carbon alpha to an aromatic ring

○— bound to a carbon beta or further from an aromatic ring

Example:

(naphthalene-CH₃) = ⬡ + ◯ + ○—CH₃