A SECOND LOOK AT THE REDUCTIVE ALKYLATION OF COAL AND AT THE NATURE OF ASPHALTENES

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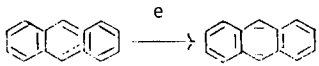
I am greatly honored to receive the 1976 Storch Award. It seems that I am the beneficiary of Dr. Storch's achievements on two counts: first as the recipient of the Award established as a memorial to him, and second for having the good fortune to work in the research environment created by Dr. Storch and continued by his successors.

I would like to take this opportunity to update our work on the reductive alkylation of coal and on the nature of asphaltenes. During the past two years I have had occasion to present these topics in formal and informal talks and to benefit from questions raised and criticisms offered. The purpose of this paper is to deal with some of these questions and to suggest further work in these areas of coal research.

Reductive Alkylation of Coal

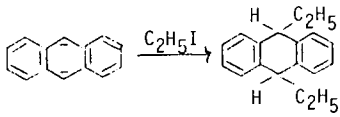
Reductive alkylation of coal (1,2) involves essentially four types of reactions:

1. Addition of electrons to the aromatic hydrocarbon structures of coal (illustrated by anthracene) to form the corresponding aromatic hydrocarbon anions.
2. Cleavage of ether bonds to form the corresponding phenolate anions.
3. C-alkylation of the aromatic hydrocarbon anions.
4. O-alkylation of the phenolate anions.



$$R\text{-}O\text{-}R \xrightarrow{e} R\text{-}O^- + R^- \qquad 2)$$

Coal Anion



$$R\text{-}O^- + R^- \xrightarrow{C_2H_5I} R\text{-}OC_2H_5 + RC_2H_5 \qquad 4)$$

Reductively Alkylated Coal

The products formed according to equations 1 and 2 represent the coal anion, those formed according to equations 3 and 4, the reductively alkylated coal. It must be emphasized that hydroxylated aromatic compounds such as naphthol or anthranol do not undergo C-alkylation. The negative charge in the anion $Ar\text{-}O^-$ is partially distributed over the aromatic ring and thereby prevents further addition of electrons to the latter. Reductive alkylation of aromatic hydrocarbons in coal can take place only when these aromatic hydrocarbons are separated from aromatic hydroxy compounds by sp^3 carbons or other linkages that do not transmit resonance effects. Reductive alkylation of $Ar\text{-}O^-$ anions may take place if the aromatic ring system, Ar, is large enough to accommodate two or more negative charges.

Effect of Alkali Metal on the Reductive Alkylation of Coal

A criticism often voiced with regard to the mechanism (equations 1-4) proposed for the reductive alkylation of coal runs along the following lines.

Reductive alkylation of coal probably involves a variety of reactions including free radical and elimination reactions. For example, reductive alkylation removes about half of the sulfur and one third of the nitrogen present in the untreated coal (1,2). Removal of sulfur is probably due to conversion of dibenzothiophene structures to biphenyl ring structures with elimination of sulfur as H_2S (3). In a similar way, removal of nitrogen may be due to conversion of carbazole to biphenyl ring structures with elimination of nitrogen as NH_3 (4). It might be misleading therefore, to assume that only the reactions described by equations 1-4 are taking place during reductive alkylation of coal.

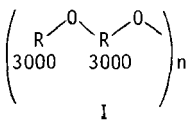
Though this criticism is justified, we must not lose sight of the fact that, on the whole, equations 1-4 accurately describe the main reactions that are taking place during reductive alkylation of coal. A good indication that C-alkylation of aromatic hydrocarbon anions plays a major role is the effect of alkali on the extent of alkylation. In the presence of lithium, 7.2, while in the presence of potassium, 8.8 alkyl groups per 100 carbon atoms are added to the coal anion (1).

At the time we reported this result (1) we had no explanation as to why potassium should be more effective than lithium. Since then we have learned that a similar effect was observed and reported by P. W. Rabideau and R. G. Harvey in a paper entitled "A Novel Metal Effect in the Reductive Methylation of Naphthalene" (5). These authors found that methylation of naphthalene in liquid ammonia in the presence of lithium yielded predominantly the monomethyl while methylation in the presence of sodium produced the dimethyl derivative as the major product. The authors attributed this difference to the fact that the lithium-naphthalene ion pair exists as a solvent separated ion pair, while the sodium-naphthalene ion pair is present as an intimate (contact) ion pair. Now the naphthalene anion in the sodium-naphthalene ion pair is less susceptible to protonation by the solvent than the naphthalene anion in the lithium-naphthalene ion pair. Consequently, the naphthalene anion in the sodium ion pair adds two methyl groups while the napthalene anion in the lithium ion pair, being more susceptible to protonation, adds one proton and one methyl group. In applying these results to coal, one could say that the coal (aromatic hydrocarbon) anion in the potassium-coal ion pair is less susceptible to proton attack than the coal anion in the lithium-coal ion pair. Consequently the former is more extensively alkylated than the latter.

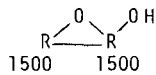
Ether Cleavage vs. C-Alkylation

The following question is always raised in discussions on the conversion of coal to a benzene soluble product by reductive alkylation: Is the conversion of coal to a benezene soluble product due to C-alkylation (addition of alkyl groups to the aromatic hydrocarbon anions) or due to ether cleavage? I do not think that this question can be decided on the basis of experimental evidence available to date.

To illustrate this point, we may consider two extreme coal structures, I and II.

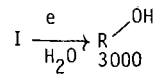


I

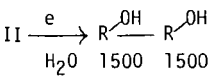


II

In both cases, ether cleavage yields units with the same molecular weight, i.e. 3000:



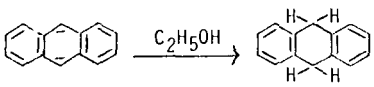
5)



6)

Those who prefer structure I argue that without ether cleavage, C-alkylation could not impart benzene solubility either to the original coal or to the cleavage products. Those who prefer structure II believe that C-alkylation suffices to convert II into a benzene soluble product. In other words, if coal had a polymeric structure such as I, then C-alkylation would be necessary but not sufficient to convert coal into a benzene soluble product. Ether cleavage in addition to C-alkylation would be required to make coal, having a structure such as I, benzene soluble.

Though we do not know whether ether cleavage is necessary to convert coal into a benzene soluble product, there is experimental evidence (1) that ether cleavage alone is not sufficient. When coal is converted to the coal anion, ether cleavage takes place (equation 2) along with formation of aromatic hydrocarbon anions (equation 1). When the coal anion is now treated with a proton donor such as ethanol, protons are added to the anions to give the corresponding hydrocarbons and phenols according to equations 3' and 4' (analogous to equations 3 and 4).



3')

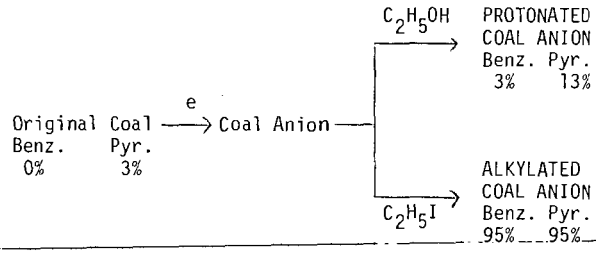
$$R\text{-}O^- + R^- \xrightarrow{C_2H_5OH} R\text{-}OH + HR$$

4')

In contrast to the alkylated coal anion which was 95% soluble, the protonated coal anion was only 3% soluble in benzene. These results along with the benzene and pyridine solubilities of the starting coal and treated coals are summarized in Figure 1.

Figure 1

Benzene and Pyridine Solubility of Original and Treated Coals



From Figure 1 it seems that alkylation of the coal anion is necessary to convert coal to a benzene soluble product.

Ether Cleavage and Pyridine Solubility

When we first published our work on solubilization of coal by reductive alkylation we were primarily interested in the benzene solubility of the treated coal. Since then we have found (6,7) that pyridine soluble, benzene insoluble material is present in coal conversion products such as SYNTHOIL and solvent refined coal (SRC). In light of these findings, the increase in pyridine solubility indicated in Figure 1 assumes a new importance. This increase in pyridine solubility from 3% to 13% may not seem significant, but there is reason to believe that considerably higher pyridine solubilities may result if coals of higher oxygen content and lower molecular weight were subjected to ether cleavage. This prediction is based on the following considerations.

The increase in pyridine solubility of the protonated coal anion over the original coal (Figure 1) is probably due to depolymerization and/or increase in phenolic hydroxyl groups according to equations 5 and/or 6. Pyridine solubility will also be dependent on molecular weight, i.e., solubility will increase with decreasing molecular weight.

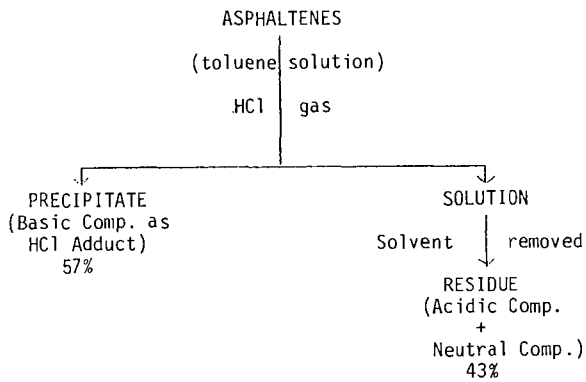
Now the experiments summarized in Figure 1 were carried out with Pocahontas coal, a coal of relatively high molecular weight of about 3000 (1) and low (3%) oxygen content. Recent work by J. Y. Sun and E. H. Burke (8) has shown that Southern Illinois coal with an oxygen content of 9%, i.e., three times that of Pocahontas coal has a molecular weight of only 770 or one fourth that of Pocahontas coal. It would be interesting to determine the effect of ether cleavage on pyridine solubility in Southern Illinois and similar coals of high oxygen content and low molecular weight. It is conceivable that ether cleavage may suffice to convert these coals into pyridine soluble products.

Acid-Base Structure of Coal-Derived Asphaltenes

Asphaltenes, operationally defined as material soluble in benzene and insoluble in pentane, are key intermediates in conversion of bituminous coals to oil (9,10). We found (11) that asphaltenes, isolated in 40% yield from a coal liquefaction (SYNTHOIL) product, contained hydrogen bonded acid-base complexes and that these complexes could be separated into their acidic and basic components indicated in Figure 2.

Figure 2

Asphaltene Components



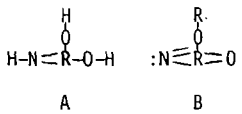
Based on ultimate analyses summarized in Table 1, and other experimental data (11),

Table 1

Ultimate Analyses and Molecular Weights of Asphaltenes and Their Acidic and Basic Components

Material	Composition (%)						Molecular weight
	C	H	O	N	S	Cl	
Asphaltenes	87.43	6.52	3.52	2.16	0.37		417
Acidic component	87.40	7.04	3.39	0.99	0.51	0.67	550
Basic component (as HCl adduct)	83.35	5.78	3.48	2.72	0.53	4.14	
Basic component (calc. HCl-free)	87.06	5.91	3.64	2.84	0.55		368

we arrived at the composite structures A and B for the acidic and basic components:



A B

The essential features of these structures may be summarized as follows. The oxygen in the acidic component is present as phenolic hydroxyl and the nitrogen as acidic nitrogen, as in pyrrole. The oxygen in the basic component is present as ring or ether oxygen and the nitrogen as basic ring nitrogen as in pyridine. Complex formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups.

It has been pointed out that inspection of Table 1 shows that the nitrogen content (2.84%) of the basic component is too low to account for one nitrogen per molecule of number average molecular weight of 368. Given a molecular weight of 368 and assuming one nitrogen per molecule as indicated in the composite structure B, the nitrogen content should be 3.95%. Our explanation is that the low nitrogen content is due to the difficulties involved in determining nitrogen in certain compounds (12). The standard Dumas method used for determining the nitrogen content of the basic component may not have been adequate for this purpose.

Acid-Base Structure of Coal

We suggested (11) that coal may have an acid-base structure analogous to that of asphaltenes on the basis of the following considerations.

Our experimental data indicate that the acidic component contains all and the basic component none of the acidic (deuterium exchangeable) hydrogen present. This result precludes the possibility of the asphaltenes having an amphoteric structure. That a complex mixture of compounds such as asphaltenes is composed of acids and bases is an unexpected result. It suggests that coal, too, may have an acid-base structure contrary to the generally accepted view that acidic and basic functional groups are randomly distributed over the whole coal molecule. It seems extremely unlikely that conversion of coal to asphaltenes could change such a random distribution of acidic and basic functional groups into one where these groups are segregated, that is, where acidic and basic functional groups are attached to different molecules.

The acid-base structure of coal has been questioned. The objections and replies may be summarized as follows.

1. Those who object to an acid-base structure point to the fact that there are strict steric requirements as to bond lengths and bond angles for hydrogen bonding to take place. It seems unlikely that such requirements could be met by the large and complex structural units that are present in coal.

This objection is not necessarily valid. Complex hydrogen bonded structures are ubiquitous in biological material derived from plant and animal life. These hydrogen bonded structures, present at the start of the decay process, retain their hydrogen bonded configuration during coalification. There is no need to invoke any special rearrangements to explain the formation of these hydrogen bonds.

2. If the acidic and basic components in coal were held together only by hydrogen bonds, then it should be possible to break these bonds and to solubilize coal by treatment with polar solvents such as pyridine. Since this cannot be done, the acidic and basic components of coal must be linked by other bonds, probably covalent bonds.

This is a valid objection and must be taken into consideration when proposing coal structures containing acidic and basic components.

3. The extrapolation from asphaltene to coal structure is not justified in view of the fact that the asphaltenes represent only 40% of the liquified coal. These asphaltenes, it is argued, are clevage products and have a low molecular weight compared to that of the original coal. It is, therefore, not surprising that these relatively small units do not contain both acidic and basic functional groups. The situation may be entirely different for the large coal molecules which may contain both acidic and basic functional groups in the same molecule.

Perhaps some experimental evidence for or against this objection could be obtained by dissolving reductively alkylated coal in toluene and passing dry HCl gas through the solution as described in the case of the asphaltenes (Figure 2). Formation of an HCl-adduct and analysis of this adduct may answer the question as to whether large molecular weight basic components are present in coal. No acidic components would be present under these conditions since all of the phenolic hydroxyl groups would have been alkylated.

Coal Structure and the Conversion of Coal to Pyridine Soluble Products

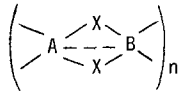
In the past it has often been tacitly assumed that the benzene insoluble material in coal conversion products consisted essentially of unreacted coal. We found (6,7) that this assumption is not justified. The benzene insoluble material is soluble in pyridine and soluble in the product oil where it exerts a large effect on viscosity. We assumed that this benzene insoluble, pyridine soluble material is intermediate between coal and benzene soluble, pentane insoluble asphaltenes; no longer coal and not yet asphaltenes. To differentiate the pyridine soluble, benzene insoluble material from the benzene soluble, pentane insoluble material we called the former "pre-asphaltenes" (7). It was recently found (13) that benzene insoluble, pyridine soluble material is formed in the presence of hydrogen donor solvents at elevated temperatures in solvent refined coal (SRC) processes, i.e. in the absence of an added catalyst. The contact time required for almost quantitative conversion of coal to pyridine soluble material is very short, of the order of minutes.

This pyridine soluble conversion product, is undoubtedly much closer related to coal than the benzene soluble, pentane insoluble asphaltenes. It will be interesting to determine whether it also contains acidic and basic components.

In that case one could visualize coal structures where hydrogen bonded acidic and basic components are linked by covalent bonds as indicated in Figure 3. Similar structures have been suggested by Koelling and Hausigk (14).

Figure 3

Coal Structures



$X = -(CH_2)_n-,\ -\overset{R}{\overset{|}{C}}H-,\ -O-,\ -CH_2-O-$

Work by Koelling and his coworkers (15,16) indicates that hydrogenolysis of coal may involve ether cleavage. They found that bituminous coal was converted in 1,2,3,4-tetrahydroquinoline at 300°C to a product 55% soluble in pyridine and having a molecular weight of 593. The authors attribute the solubilization of coal to cleavage of ether bonds on the basis of experiments with the following two groups of model compounds: (a) toluene, α-methylnaphthalene, diphenylmethane, diphenyl and (b) phenol, diphenylether, phenylbenzylether, dibenzylether. Treatment with tetrahydroquinoline at 390°C left the compounds in group (a) as well as phenol and diphenylether of group (b) unchanged. Phenylbenzylether and dibenzylether, on the other hand, were quantitatively converted to phenol and toluene and to benzylalcohol and toluene respectively.

Evidence, based on the work of Heredy and Neuworth (17) indicates that the aromatic units in coal are linked by methylene bridges. In that case, conversion of coal to a pyridine soluble material by hydrogenolysis may be attributed to thermal cleavage of methylene C-C bonds followed by addition of hydrogen to the cleavage products.

Our work on the other hand, indicates that coal can be solubilized without breaking any C-C bonds and that cleavage of C-O ether bonds may be required to convert coal to a pyridine soluble product. On that view, conversion of coal to a pyridine soluble product by hydrogenolysis may be due to thermal cleavage of C-O ether bonds followed by addition of hydrogen to the cleavage products.

If conversion of coal to a pyridine soluble material is due to ether cleavage alone then electron addition followed by protonation (equation 7) should give the same product as hydrogenolysis in the presence of a donor solvent (equation 8).

$$R\text{–}O\text{–}R \xrightarrow[\text{Room Temp.}]{e,H_2O} R\text{–}OH + RH \qquad 7)$$

$$R\text{–}O\text{–}R \xrightarrow[400^{o}C]{\text{H-Donor}} R\text{–}OH + RH \qquad 8)$$

A comparison of pyridine soluble products obtained by reactions 7 and 8 should help answer the question whether or not cleavage of ether bonds is essential for the conversion of coal to a pyridine soluble material.

Conversion of coal to pyridine soluble material can be accomplished by phenol,BF_3 depolymerization (17), reductive alkylation (1,2) and hydrogenolysis in the presence of a hydrogen donor solvent (13). An investigation of the products obtained by these methods in conjunction with model compound experiments should lead to a better understanding both of coal structure and the mechanism of coal conversion.

References

1. H. W. Sternberg, C. L. Delle Donne, P. Pentages, E. C. Moroni and R. E. Markby, Fuel, 50, 432 (1971).

2. H. W. Sternberg and C. L. Delle Donne, Fuel, 53, 172 (1974).

3. H. W. Sternberg, C. L. Delle Donne and I. Wender, Fuel, 47, 219 (1968).

4. J. J. Eisch, J. Org. Chem., 28, 707 (1963). (I am indebted to Dr. Leon M. Stock, University of Chicago, for calling my attention to this reaction.)

5. P. W. Rabideau and R. G. Harvey, Tetrahedron Letters, No. 48, 4139 (1970).

6. H. W. Sternberg, R. Raymond and S. Akhtar, "SYNTHOIL Process and Product Analysis", Symposium on Hydrocracking and Hydrotreating Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society, Philadelphia Meeting, April 6-11, 1975.

7. H. W. Sternberg, R. Raymond and F. K.Schweighardt, "The Nature of Coal Liquefaction Products", Symposium on Progress in Processing Synthetic Crudes and Resids Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society, Chicago Meeting, August 24-29, 1975.

8. J. Y. Sun and E. H. Burke, "Coal Molecular Weight Distribution by GPC", in "Fundamental Organic Chemistry of Coal", Proceedings of a Workshop Sponsored by the National Science Foundation Held at The University of Tennessee, Knoxville, July 17-19, 1975.

9. S. Weller, M. G. Pelipetz and S. Friedman, Ind. Eng. Chem., 43, 1572 (1951); Ibid., p. 1575.

10. B. J. Liebenberg and H. G. J. Potgieter, Fuel, 52, 130 (1973).

11. H. W. Sternberg, R. Raymond and F. K. Schweighardt, Science, 188, 49 (1975).

12. W. R. Kirner, Ind. Eng. Chem., Anal. Ed., 7, 294 (1935).

13. D. D. Whitehurst, Mobil Research and Development Corporation, Private Communication.

14. G. Koelling and D. Hausigk, Brennstoff-Chemie, 50, 1 (1969).

15. R. Bruecker and G. Koelling, Brennstoff-Chemie, 46, 41 (1965).

16. D. Hausigk, G. Koelling and F. Ziegler, Brennstoff-Chemie, 50, 8 (1969).

17. L. A. Heredy and M. B. Neuworth, Fuel, 41, 221 (1962); L. A. Heredy, A. E. Kostyo and M. B. Neuworth, Fuel, 43, 414 (1964); L. A. Heredy, A. E. Kostyo and M. B. Neuworth, Fuel, 44, 125 (1965).

ON THE CHEMICAL NATURE OF THE BENZENE INSOLUBLE COMPONENTS OF SOLVENT REFINED COALS

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INTRODUCTION

The present emphasis on the conversion of coal to substitute petroleum fuels has led to several alternative processes which are now being investigated.

Among the many processes being considered is the solvent refining of coal (SRC) in which coal is treated at an elevated temperature in the presence of a hydrogen-donor solvent and hydrogen gas to lower the sulfur content of the coal, remove the mineral matter, and convert it into a low melting solid which can be solubilized in simple organic solvents. The work reported here is concerned with developing a fundamental understanding of the chemistry of this process.

Little is known at present as to the exact mechanisms by which the coal is transformed into soluble form, the detailed chemical structure of the soluble product, or even of the parent coal. It is known that many coals are easily solubilized and others are more difficult (1).

A common means of fractionation and characterization of SRC products is through solvent extraction. The major classifications referred to include oils (hexane soluble compounds), asphaltenes (benzene soluble-hexane insoluble compounds), and less soluble materials (pyridine soluble-benzene insoluble compounds). Of these, the asphaltenes and pyridine soluble-benzene insoluble materials are believed to be responsible for high viscosity, solvent incompatibility, and processing difficulties.

Often the extent of coal conversion is measured in terms of the solubility characteristics of the product, and mechanisms for coal conversion involving such classifications have been proposed (2-4). The reported mechanisms conclude that asphaltenes are a necessary product of coal conversion and that they are the primary precursors of oils (2-4).

Some recent work has been reported (5-8) on further fractionation and characterization of SRC products. However, the major emphasis has primarily concerned oils and asphaltenes. We will show that at low conversions of coal, the concentration of benzene insoluble compounds can amount to 70-80% of the total SRC, and therefore these are of great importance in understanding the mechanisms of coal conversion.

EXPERIMENTAL

The molecular weights and elemental analyses of various coal products were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee, and Spang Microanalytical Laboratory, Ann Arbor, Michigan.

The IR spectra were measured on a Perkin-Elmer 237B grating infrared spectrophotometer. The NMR spectra were measured on a Varian A-60 spectrophotometer for H-NMR; ^{13}C NMR were determined using a Varian XL-100 spectrophotometer by G. Mateescu of Case Western Reserve University, a Varian CFT-20 spectrophotometer by G. Gray at Varian, and a JEOL FX-60 spectrophotometer by R. H. Obenhauf of JEOL.

A duPont 950 thermogravimetric analyzer was used to determine the weight vs. temperature profile of coals and coal products. Polarographic reductions were performed by F. Rogers of the Department of Aerospace and Mechanics, Princeton University. The apparatus used was the Princeton Applied Research (PAR) Model 174 Polarographic Analyzer, using a dropping mercury electrode in the differential pulse mode.

All extractions were performed using a Soxhlet extraction apparatus with controlled N_2 or Argon atmosphere. Paper thimbles were used and extractions were carried to exhaustion (generally ~17 hr.).

The conversion apparatus has been described in detail elsewhere (10,11). Briefly, it consists of a stirred batch autoclave in which solvent is heated to reaction temperature. A 1:1 coal: solvent slurry is then injected. To quench, water under pressure is forced through a cooling coil in direct contact with the vessel contents. Conversion times as short as 0.5 min. at reaction temperature are routinely achieved.

The synthetic solvent has also been described in detail elsewhere (10,11). It is ~2% 4-picoline, 17% p-cresol, 43% tetralin, and 38% 2-methyl-tetralin.

RESULTS AND DISCUSSION

In order to obtain a fundamental understanding of the chemical nature of coal and the organic mechanisms involved in its conversion to soluble form, we felt it necessary to develop a method of chemical fractionation of the whole SRC.

The use of extraction (to separate the pentane soluble and benzene soluble fractions) has a very limited utility from a fundamental chemical standpoint. The solubility of different substances is not only a function of the molecular weight, carbon-hydrogen skeleton, and chemical functionality, but also depends on interactions with other soluble species which can act as cosolvents. Therefore, the same compound can appear as "oil" or as "asphaltene," depending upon the presense or absence of other species in coal liquids. Even in

very carefully performed extractions or precipitations, some products will often be distributed between extract and residue because of limited solubility.

Accordingly, a liquid chromatographic procedure for chemical fractionation of SRC was developed. This method, which we refer to as SESC, uses silica as the stationary phase, and is described elsewhere (9,10). To the best of our present understanding, the elution solvents, the resultant chemical classes obtained with this method, and the relationships between the fractionation solubility classifications, are shown in Figure 1. As can be seen, asphaltenes are primarily monofunctional compounds, and oils contain appreciable amounts of non-hydrocarbons (primarily ethers and thioethers).

The benzene insoluble materials, although less completely defined, are clearly distinguished from asphaltenes and oils by a higher degree of functionality. Our preliminary evidence indicates that this higher functionality is primarily in the form of more -OH groups per molecule, as will be discussed later. Accordingly, we propose the name asphaltols for this class of compounds, and will refer to them as such in this report.

It is commonly believed that in order to convert coal eventually to oils, a sequence of reactions must occur with increasing heteratom removal at each stage of the sequence. A generalized scheme, including definitions of terms used in this report and approximate heteroatom content at various stages of conversion, is outlined below:

Coal →	Insoluble Solids →	Pyridine Soluble Compounds →	Benzene Soluble Compounds →	Hexane Soluble Compounds
Terms	Residues & Char	Asphaltols	Asphaltenes	Oils
Heteroatom Content	>10% res. 1-10% char	5-10%	~2%	1% or less

If one assumes a sequential reaction of coal → asphaltene → oil, then a kinetic description of the progress of the reaction can be obtained by plotting the composition of the soluble product vs. the yield of total soluble product. Earlier reports (2-4) indicated that asphaltenes were primary products from coal, and indeed if the reported data are plotted in this way, this assumption appears to be valid (see Figure 2). These data, however, were obtained in the absence of any hydrogen donor solvent.

Since asphaltols were not accounted for in the reported kinetic studies (2-4), we conducted for comparison a series of coal conversions using West Kentucky 9,14 coal using procedures previously described (10,11). The results shown below indicate that at low coal conversion levels, asphaltols are the predominant products.

Run #	Extract	9	10	7	12
Reaction Time (min.)	0	1.3	0.5	40	417
% O in SRC	9.47	7.25	6.68	5.15	2.93
wt. % Hexane Soluble (oils)	8.3	5.1	7.1	10.3	32.1
wt. % Benzene Soluble (asphaltenes)	11.7	8.6	13.5	18.8	28.4
wt. % Benzene Insoluble (asphaltols)	80.0	86.3	79.3	70.8	39.5
wt. % SRC Yield	28.0	76.1	46.8	73.2	61.1
wt. % Conversion to soluble form	28.0	78.2	50.0	93.0	96.1

When these data are plotted in the above described manner (Figure 3), it can be seen that the commonly accepted sequential description for the conversion of coal to oils through asphaltenes appears not to be operative when hydrogen donor solvents are present. A more correct interpretation of the conversions involved appears to be that asphaltols are predominant, primary products (some asphaltenes and oils are formed in parallel from the coal), and the asphaltols are then converted in a parallel fashion to asphaltenes and oils, with a small preference for the formation of oils.

Early in the conversion process (<5 min.) we find, by gel permeation chromatography, that the product in solution may be up to 40% high molecular weight (>2,000 MW) or very strongly associated molecules. These high molecular weight species would be classified as asphaltols and are found in fractions 9 and 10 of our fractionation procedure (SESC). The relative concentration of this material then rapidly declines, producing material in the 300-900 MW range. In coal extractions, this material is in the THF insoluble, pyridine soluble portions. Typical results for the conversion of Wyodak coal at 800°F in H_2 and our synthetic solvent are shown below:

	Wt. % of Original Coal		
Time, min.	Low Molecular Weight	High Molecular Weight	Total
1.20	16.86	10.97	27.80
3.60	15.41	6.13	21.53
6.00	44.32	8.48	52.80
19.50	44.99	6.70	51.69
38.00	65.77	6.87	72.64
74.00	66.45	4.79	71.24
137.50	70.54	4.03	74.57

Because of the predominance of asphaltols during the initial stages of coal conversion, we have begun detailed chemical characterization of these materials as well as kinetic and mechanistic studies on their conversion under typical solvent refining conditions.

Isolation of the materials was accomplished by preparative SESC or selective extractions. Three SRC's produced in pilot plants were studied; Illinois #6 and West Kentucky 9,14 SRC's, produced by the pilot plant operated by Catalytic, Inc., for Southern Services, Inc. at Wilsonville, Alabama, and Wyodak SRC, produced by Hydrocarbon Research, Inc. in Trenton, New Jersey. The quantity of the fractions isolated, their corresponding elemental analyses and molecular weights are shown in Figures 1 and 2, for West Kentucky and Wyodak, respectively. The emperical formulae for various fractions are also shown.

We have developed semiquantitative correlations between the SESC fractionation and solubility classification as shown in the tables. An interesting consequence is the fact that the partitioning of a given SESC fraction into either benzene soluble or benzene insoluble material is a function of the original coal as well as the degree of conversion. For example, with West Kentucky SRC, oils constitute SESC fractions 1, 2 and 1/2 of fraction 3. Asphaltenes constitute 1/2 of fraction 3, fraction 4, and 1/2 of fraction 5. With Wyodak SRC, fraction 5 is completely benzene insoluble.

In comparing the composition of the various fractions, it can be seen that West Kentucky SRC fractions have higher molecular weights for asphaltols than for oils or asphaltenes; however, with Wyodak SRC the molecular weights are approximately the same. With both SRC's the asphaltols have >3 oxygen atoms per molecule, indicating a high degree of functionality. An increasing -OH content with increasing fraction number can be seen by infrared spectroscopy as shown in Figure 4.

To gain understanding as to the type of molecules that can be found in the various asphaltol fractions, we have conducted SESC analyses of a number of model compounds, and have tabulated below in which fraction they appeared:

<u>Fraction 5 - Basic Nitrogen and Di and Tri Functional Oxygen</u>

Chrysin
Julolidine
N,N'-di-(2-naphthyl)-p-phenylene diamine
Naphthoflavone
Veratrine (mix of alkaloids)*
Anthrarobin

<u>Fraction 6 - Polyfunctional</u>

8-hydroxyquinoline
Rutin
nicotinamide

<u>Fraction 7 - Polyfunctional</u>

(No models could be found)

<u>Fraction 8 - Polyfunctional</u>

6,13 dihydrodibenzophenezine

Fraction 9 - Polyfunctional

Veratrine (mix of alkaloids)*
Phenolphthalein

* Alkaloids were found in both fractions 5 and 9.

All model compounds occurring in these fractions have multiple functionality.

The aromatic content of the various SESC fractions are shown in Table 3. A general trend appears to be that the asphaltols have less aromatic hydrogen and aromatic carbon than the less functional materials, and more closely resemble the composition of the parent coal (12).

It should be noted also that polarographic analysis of asphaltols indicates that the number of condensed aromatic rings (more than 2 rings) is quite small.

A distinguishing characteristic of asphaltols as compared to asphaltenes or oils is their behavior on pyrolysis in inert atmospheres. In Figure 5 it can be seen that asphaltols yield up to 80% char on pyrolysis in inert atmosphere. This char formation occurs in the temperature regime of coal liquefaction and could well contribute to high coke make during SRC processing. Attempted duplication of this behavior with model compounds indicated that increasing char formation tendency paralleled increasing -OH content; however, no model compounds could be found that could produce char at the magnitude found for asphaltols.

Based on the above information, a formal average structure for West Kentucky asphaltol (SESC 8) can be constructed as shown in Figure 6. Structures of this type can easily aromatize, with elimination of H or through skeletal rearrangement. If one attempts a similar treatment of the data for Wyodak asphaltols, a much more condensed polycyclic aliphatic structure must be proposed. The structure of all fractions of SRC change with increased severity of coal conversion. The products generally increase in both total aromatic and highly condensed aromatic ring contents; H/C ratio and total hydrogen contents decrease (11).

To gain insight into the chemistry and reactivity of these highly functional materials, several fractions or concentrates were converted under typical SRC processing conditions, and the products analyzed. The results are presented in Table 4. It can be seen that asphaltols, relative to asphaltenes, tend to produce less oil and more pyridine insolubles (char) and consume less hydrogen, but an important observation is that both asphaltenes and asphaltols produce <u>all</u> classes of products. Hydrogen consumption appears to correlate with the production of oils and solvent-range material, not gases. These general observations have been confirmed by additional runs, not shown here.

In conclusion, we would like to reemphasize the importance of asphaltols in the initial stages of coal liquefaction. Their propensity

toward char formation at temperatures comparable to liquefaction temperatures, their high degree of functionality, and the fact that they are the predominant, primary products of coal, indicate that much valuable information which could relate to criticalities in the SRC process could be obtained by a more thorough understanding of their chemistry and structure.

ACKNOWLEDGEMENTS:

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REFERENCES:

[1] U. S. Bureau of Mines 646.

[2] M. Pelipetz, E. M. Kuhn, S. Friedman and H. H. Storch, Ind. & Eng. Chem. 40 1259, (1948).

[3] S. Weller, E. L. Clark and M. G. Pelipetz, Ind. & Eng. Chem. 42 334 (1950).

[4] S. Weller, M. G. Pelipetz, E. S. Friedman, Ind. & Eng. Chem. 43 1572 (1951).

[5] Sternberg, H. W., Raymond, R., Schweinghardt, F. K., SCIENCE, 1975, 188, 49.

[6] Leete, E., J. AMER. CHEM. SOC., 1961, 83, 3645.

[7] Given, P. H., Cronauer, D. C., Spakman, W., Lovell, H. L., Davis, A., Biswas, B., FUEL, 1975, 54, 34.

[8] Given, P. H., Cronauer, D. C., Spakman, W., Lovell, H. L., Davis, A., Biswas, B., FUEL, 1975, 54, 40.

[9] M. Farcasiu, FUEL, in press (1976).

[10] M. Farcasiu, T. O. Mitchell, and D. D. Whitehurst, 1st Yearly Report, RP-410-1 to EPRI, in press (1976).

[11] T. O. Mitchell and D. D. Whitehurst, ACS Meeting, San Francisco, August, 1976.

[12] Data on the aromatic content of coals will be published in the near future.

Figure 1

CHEMICAL FRACTIONATION OF SRC VIA MOBIL'S SESC PROCEDURE

Classical Description	Fraction	Elution Solvent	Major Compounds
Oils (1-3)	1	Hexane	Saturates
	2	Hexane/15% Benzene	Aromatics
	3	Chloroform	Polar aromatics; nonbasic N, O, S-heterocyclics
Asphaltenes (3-5)	4	Chloroform/10% Et_2O	Simple phenols
	5	Et_2O/3% EtOH	Basic nitrogen heterocyclics, di and triphenols
Multifunctional Cpds. (5 thru 9)	6	MeOH	Highly-functional molecules (>10 wt. % heteroatoms)
	7	$CHCl_3$/3% EtOH	Polyphenols
	8	THF	Increasing O content and increasing basicity of nitrogen
	9	Pyridine	
	10		Non-eluted, unknown materials

SELECTIVITY VS. CONVERSION

2-4

No Hydrogen Donor Solvent

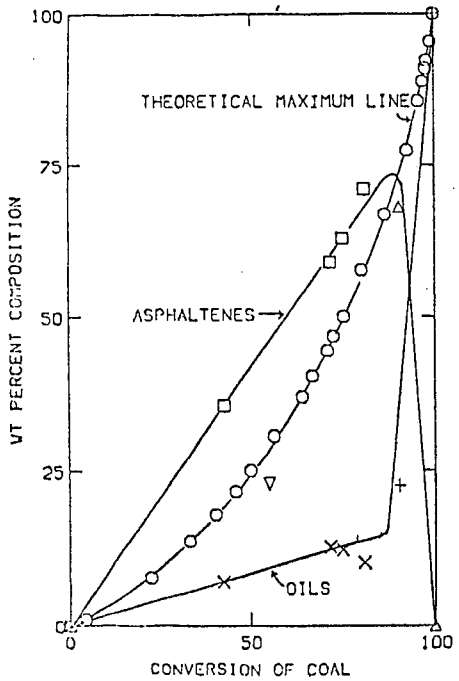


Figure 2

Hydrogen Donor Solvent

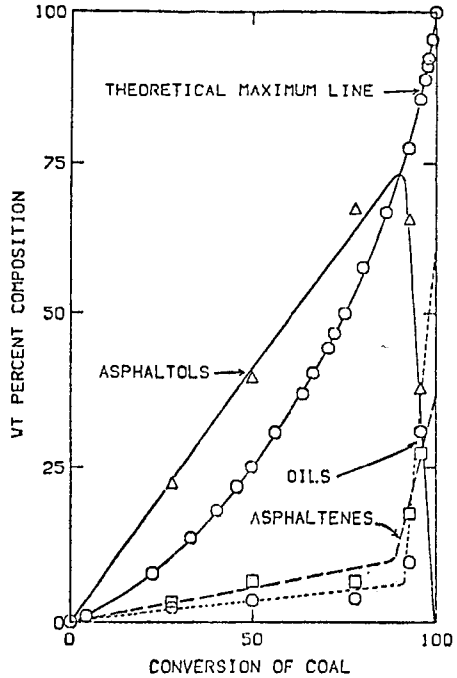


Figure 3

Figure 4

INFRARED SPECTRAL ANALYSES OF SELECTED WEST KENTUCKY SRC FRACTIONS

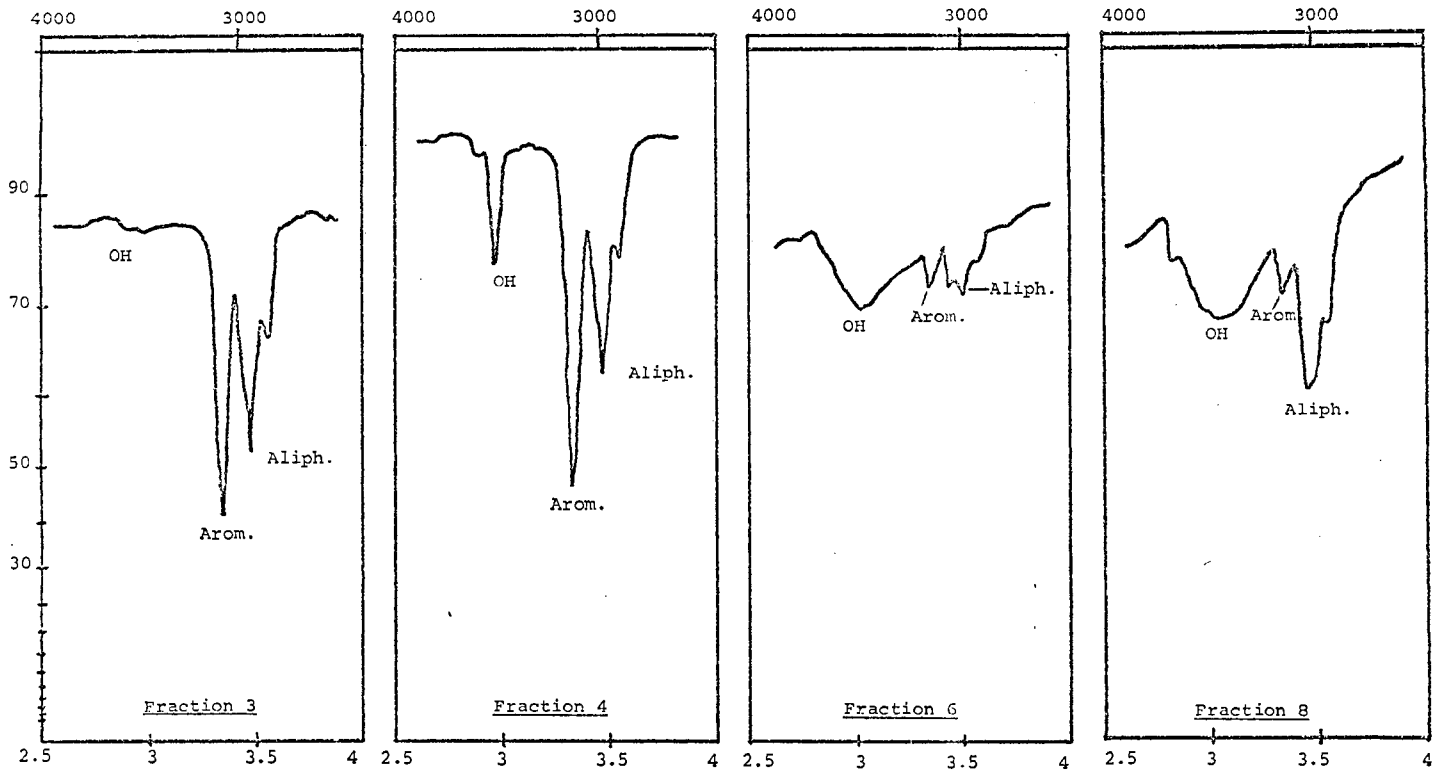
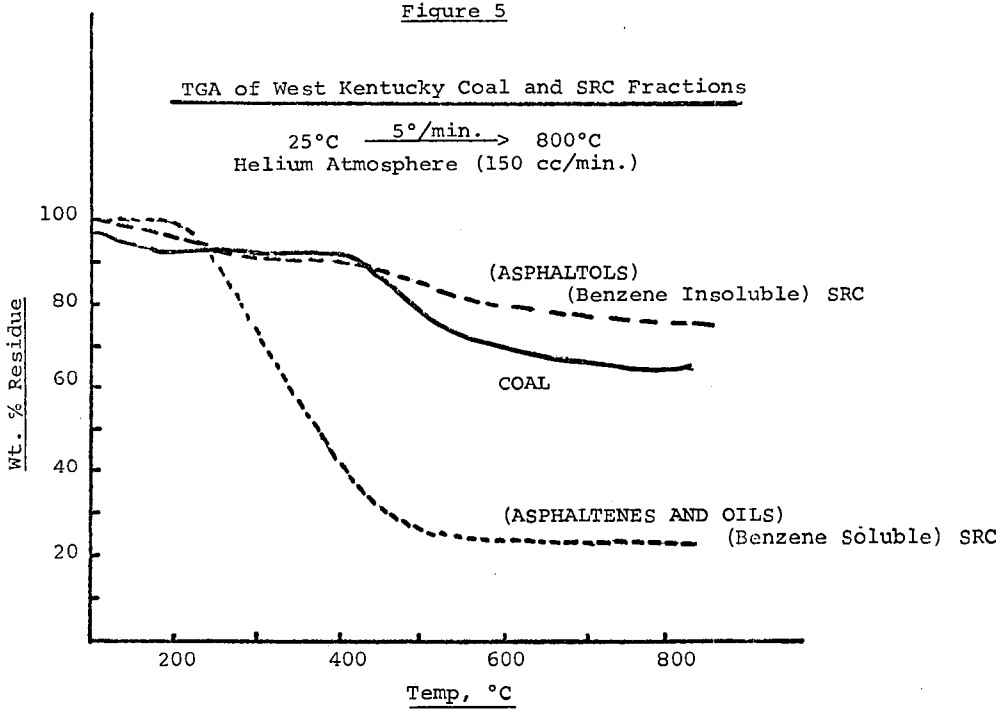


Figure 5

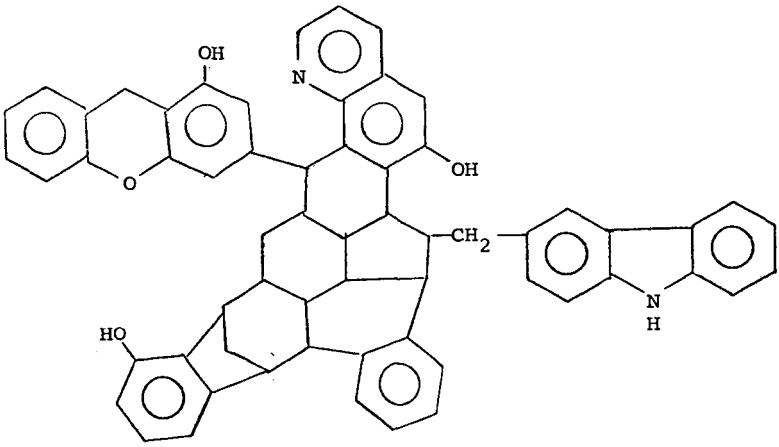
TGA of West Kentucky Coal and SRC Fractions

25°C —5°/min.→ 800°C
Helium Atmosphere (150 cc/min.)



Formal Average Structure for West Kentucky Asphaltol

(SESC 8)



$C_{61}H_{46}N_2O_4$

900 mol. wt.

73% Aromatic C

60% Aromatic H

Figure 6

Table 1

Percentage of the Fractions and Elemental Analyses of West Kentucky SRC Fractions Obtained by Preparative SESC

	Fraction	% in SRC	Elemental Analyses % C	% H	% O	% N	% S	MW	Emperical Formulae
	SRC	100	87.60	4.80	3.4	2.0	.80		
Oils (1-3)	1	0.4							
	2	15							
	3	30	91.8	5.38	1.06	0.85	0.8	325	$C_{24}H_{16}O, C_{24}H_{17}N$
Asphaltenes (3-5)	4	10.2	86.3	5.33	5.2	2.32	0.8		$C_{22}H_{17}NO$
	5	10.1	87.6[a]	5.35[a]	~2[b]	3.81	1.36	~400	$C_{30}H_{25}NO_2$
Asphaltols (5-9)	6	4.1	68.58[a]	4.82[a]	20.05[a,b]	4.77[a]	1.36		
	7	6.4	83.6	5.1	7.78	2.57	0.94	(600)[c]	$C_{41}H_{30}NO_3$
	8	10.2	81.91	5.14	7.7	2.73	1.7	~900	$C_{61}H_{46}N_2O_4$
	9	8.5	83.7[a]	4.5[a]	8.3[a,b]	2.51[a]	0.9[a]	(900)[c]	$C_{63}H_{41}N_1O_5$
	(10 non-eluted)	ca. 5							

a) results from a different preparative run
b) oxygen by difference
c) estimated molecular weight

Table 2

Percentage of the Fractions and Elemental Analyses of Wyodak SRC Fractions Obtained by Preparative SESC

	Fraction	% in SRC	Elemental Analyses % C	% H	% O	% N	% S	MW	Emperical Formulae
	1	0.5							
Oils (1-3)	2	7.6	92.14	6.40					
	3	20.8	89.7	6.15	~3	1.1		660	$C_{49}H_{41}NO$
Asphaltenes (3-5)	4	20.0	85.2	6.07	6.3	2.0		630	$C_{45}H_{38}NO_2$
	5	10.7	79.5	6.57	11.0	1.8	.76	580	$C_{40}H_{38}NO_4$
Asphaltols (5-8)	6	4.4	74.3	6.01	11.7	2.6	.65	(600)[a]	$C_{37}H_{36}NO_4$
	7	4.7	84.3	5.57	6.1	1.9			
	8	16.3	81.6	5.84	9.95	1.6		740	$C_{50}H_{43}NO_5$

a) Estimated molecular weight

Table 3

NMR Analysis of SRC Fractions

Parent Coal	SESC Fraction	Aromatic Hydrogen (9-6 ppm)	Aromatic Carbon
West Kentucky 9,14	2	82	
West Kentucky 9,14	3	81	83
West Kentucky 9,14	4	63	74
West Kentucky 9,14	5	49	65
West Kentucky 9,14	8	60	73
Wyodak	2	56	80
Wyodak	3	48	64
Wyodak	4	47	
Wyodak	5	47	53
Wyodak	6	36	
Wyodak	8	45	60

Table 4

Conversions of Asphaltenes and Asphaltols at 800°F in H_2 and Synthetic Solvent

Run	13		36		39		51	
Parent Coal	Illinois #6		Wyodak		Wyodak		Wyodak	
Feed Concentrate	Asphaltols		Asphaltenes		Asphaltols		Asphaltols	
Time, mins.	84		111		20		20	
Products (MAF)*								
Gases (C_6^-)	4.9		13.7		25.4		7.6	
Solvent Range	21.1		20.9		2.4		7.6	
SRC	61.1		58.2		62.4		65.3	
Residue	12.7		6.4		9.7		19.5	
SRC* (oils)**	25.6		34.6		7.9		12.6	
(asphaltenes)**	23.0		26.3		36.9		35.6	
(asphaltols)**	51.4		39.2		55.2		53.03	
Wt. % H-Consumption	2.2		4.7		0.6		0.6	
Wt. % H-Consumption (at 20 mins.)	1.4		1.9		0.6		0.6	
Detailed SESC Analyses*	F≠	P≠	F	P	F	P	F	P
Fraction 1	0	5.5	0.2	1.4	0	1.8	0	0
Fraction 2	0	9.9	2.1	27.7	0	3.4	0	8.3
Fraction 3	0	20.5	2.4	10.9	1.2	5.5	4.7	8.6
Fraction 4	0.6	9.4	54.7	16.3	13.7	28.7	20.6	25.8
Fraction 5	1.5	6.7	30.3	9.1	16.1	10.9	12.2	10.9
Fraction 6	3.1	4.6	6.5	22.8	7.5	6.5	6.1	3.6
Fraction 7	6.4	10.3	2.0	5.1	27.3	7.1	17.5	10.2
Fraction 8	15.4	18.4	0.6	1.7	23.3	8.7	16.1	10.4
Fraction 9	73.0	14.8	1.4	5.0	17.7	27.4	20.6	23.4

* Normalized to 100%. **These data represent only the eluted materials.

≠ F = feed; P = product

ASPHALTENES FROM COAL LIQUEFACTION

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INTRODUCTION

Asphaltenes are considered to be one of the principle intermediates in the conversion of coal to an oil product. But, over the past four decades, investigations of coal hydrogenation have only used a simple operational definition of coal-derived asphaltenes - "Benzene souble and hexane insoluble". What then can be said about these asphaltenes? What is the established laboratory procedure for isolating asphaltenes? What steps have been taken to characterize and compare asphaltenes generated from different coal liquefaction processes? Do the asphaltenes affect the physical and/or chemical properties of a coal-derived oil? These and many other questions need to be studied and some kind of answer proposed. Recent investigations indicate that asphaltenes contribute to a large measure to the viscosity of the product oil. It has even been suggested the asphaltenes are the coal monomer - the smallest unit of coal that still retains, to some degree, the spectral qualities of the whole coal. Before we go further we must establish isolation techniques that are standardized, and that do not chemically affect the asphaltene components. Once free from the virgin coal-derived oil what then are the physical, chemical and spectral properties of these "Benzene soluble-hexane insoluble" materials we call asphaltenes. When these questions have been investigated, then we may be able to answer -

What are asphaltenes?

IN THE BEGINNING

As far back as 1942 German scientists involved in coal conversion products wrote a "summary report on experiments performed at Scholnen to establish a suitable method for asphalt analysis". (1) In these early investigations the benzene soluble-hexane insoluble material was referred to as asphalts.(2,3) But, at the U. S. Bureau of Mines, the term asphalt was considered objectionable because the same word was commonly used to describe a petroleum-derived product. The petroleum product differs in some rather important aspects from coal-hydrogenation material as will be shown.

Therefore, in the United States about 1950-51, the term asphaltenes was used to define the benzene soluble-hexane insoluble components of coal-conversion products. Weller, et al. (4) detailed the isolation of the asphaltenes and, with some general modifications (5) this method has been used at the Pittsburgh Energy Research Center on a large number of samples. Recently Sternberg, et al. (6) proposed a slightly different version of separating asphaltenes from SYNTHOIL (7) centrifuged liquid products (CLP).

Let us go back to the late 1940's and early 1950's when mechanisms were first suggested for the hydrogenation of coal. Weller, et al. (4) determined that the conversion of coal to oil involved two consecutive first order reactions,

$$\text{COAL} \xrightarrow{k_1} \text{Asphaltenes} \xrightarrow{k_2} \text{OIL} \qquad (1)$$

At 400° C k_1 was reported as 25 times larger than k_2.

More recently Lieberberg and Potgieter (8) derived a more complex mechanism which includes the following simultaneous and consecutive reactions:

$$\text{COAL} \xrightarrow{k_1} \text{Asphaltenes} \xrightarrow{k_2} \text{Oil} \qquad (2)$$

$$\text{COAL} \xrightarrow{k_3} \text{Asphaltenes} \qquad (3)$$

$$\text{COAL} \xrightarrow{k_4} \text{Oil} \qquad (4)$$

Markov and Orechhin (9) on the other hand have proposed that in the initial stages of coal hydrogenation it is not the asphaltenes that are formed first, but a substance that is insoluble in benzene yet soluble in pyridine. Sternberg et al. (6) have separated these materials according to their isolation scheme and have termed these pyridine soluble-benzene insoluble materials "preasphaltenes". Now we have not only asphaltenes to contend with, but preasphaltenes as well. That brings us to one of our earlier questions - what effect do asphaltenes have on the physical properties of coal-derived oils. Figure 1,

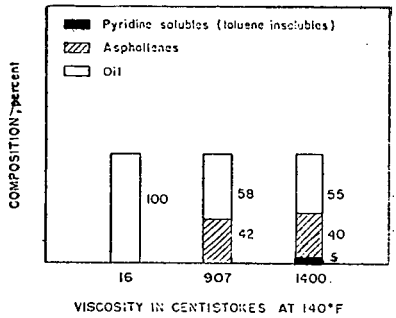

Figure 1. Effect of pyridine solubles (toluene insolubles) and asphaltenes on viscosity.

from work by Sternberg, et al. (7) shows in at least one case that the viscosity of a SYNTHOIL CLP is effected by the presence of asphaltenes and preasphaltenes. Why the effect is so large is still a matter of investigation.

ASPHALTENE ISOLATION

Before going any further we should account for the isolation of asphaltenes. Figure 2 gives

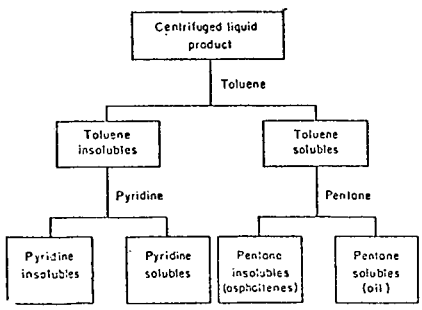

Figure 2. Fractionation scheme for centrifuged liquid product (CLP).

the fractionation scheme for asphaltenes from a SYNTHOIL CLP. The initial product as received from the process stream is hot. It is placed in a jar, quickly flushed with nitrogen, and allowed to cool to room temperature in the closed container. A portion of the sample is subjected to the isolation procedure as soon as it attains room temperature. The initial separation removes the benzene (10) insolubles. This can be accomplished by centrifugation on an analytical scale (1-3 grams), or by the Soxhlet method on a preparative scale (10-20 grams).

The recovered benzene insolubles (BI) can then be subjected to pyridine extraction to give pyridine insolubles (ash content ≈80%) and pyridine solubles (preasphaltenes). The benzene soluble portion of the CLP is reduced in volume by nitrogen flush at 30-35° C on a water bath until an approximate volume ratio of 1:1 benzene/solubles is reached. We now propose the use of n-pentane (pesticide grade for all solvents) to precipitate the asphaltenes. Pentane is added with rapid stirring, or mild (50 watt) sonication, to precipitate the asphaltenes. If a preparative method is used, a fine double thickness thimble is required, or three pentane washings on the analytical scale, with centrifugation at 2500 rpm at 20° C for 15 minutes. The asphaltenes are collected and dried at 65° C in vacuo to constant weight or redissolved in benzene (1 gram asphaltene/5 ml benzene) and freeze-dried. The later technique gives a fine, light tan material. All final products should be stored at -40° C in a glass sealed container.

The asphaltenes and preasphaltenes can be further separated by the method of Sternberg et al., (11) Figure 3. The asphaltenes are dissolved in benzene (1 gram/20 ml

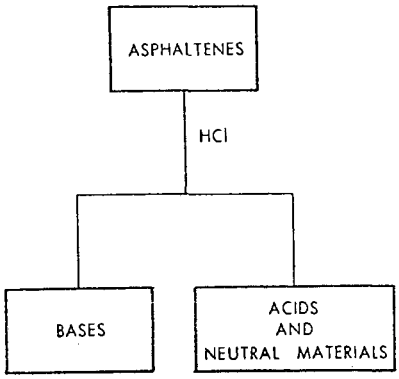

Figure 3. Asphaltene fractionation scheme.

benzene), centrifuged to collect any undissolved material, then dry HCl gas is slowly bubbled through the solution until no further evidence of precipitation is observed. This procedure forms an HCl adduct with the basic heterocyclic nitrogens (-N=). In the solution remain the neutral and acidic compounds which can be recovered by reducing the benzene volume with a nitrogen purge and freeze-drying the final solution. The nitrogen adduct can be freed of HCl by back titration in benzene with 0.5 N NaOH. This is best achieved with a freshly prepared base adduct. Prolonging this last step increases the amount of benzene insolubles left after back titration.

We have outlined these methods in some detail because, as of today, there is no standardized method for separating asphaltenes. In many cases the yield of asphaltenes can vary as much as 50% and the benzene insolubles as much as 100% by just changing the laboratory technique.

Our method may not be the best, but we find it to be reproducible to within 3%, and by using centrifugation techniques losses are less than 2% because only solutions are transferred.

CHARACTERIZATION OF ASPHALTENES

Husack and Columbic (12) first described a separation scheme for the characterization of the phenolic constituents of coal-derived asphaltenes by extracting with aqueous alkali and methanolic KOH (Classen alkali). They concluded that most of the oxygen content of the phenolic fractions could be accounted for by hydroxyl (OH) and that 25% added active hydrogen could be assigned to nitrogen compounds (NH). Sternberg et al.(11) some 25 years later came to the same conclusions by separating the acidic and basic components by HCl adduct formation and determining the presence of phenols, pyrroles and pyridine-like bases by thin-layer chromatography (TLC), thin-layer electrophoresis (TLE) and nuclear magnetic resonance (NMR). Sternberg has proposed that the acidic and basic components form a macro-molecular hydrogen-bonded complex upon the addition of pentane to the aromatic solution. Schweighardt, et al.(13) have investigated this hydrogen bonded complex by multi-nuclei magnetic resonance (^{1}H, ^{13}C and ^{14}N), and have confirmed that the separable acid and base components do form hydrogen bonded species with model compounds (pyridine and o-phenylphenol), as well as with each other.

The presence of phenolic (OH) functional groups in the asphaltene fraction of coal hydrogenation oils has been of considerable interest over the past 20 years. Friedman, et al. (14) were the first to quantitate the hydroxyl content by forming the trimethylsilyl ether (TMS) of the asphaltenes. The infrared analyses of the product indicated that almost all the hydroxyl groups had reacted. Their treated asphaltene contained 6.21% silicon, corresponding to a hydroxyl oxygen content equivalent to 64% of the oxygen present in the original asphaltenes.

Brown, et al. (15) have applied the TMS derivative formation to the acid and base fractions of a SYNTHOIL asphaltene and have confirmed the presence of hydroxyl (OH) by infrared and nuclear magnetic resonance. An important feature of their work is that in dilute solution (CS_2) the base components of a coal-derived asphaltene contain some OH, as evidenced in the infrared spectrum in figure 4. The OH content was confirmed by forming a

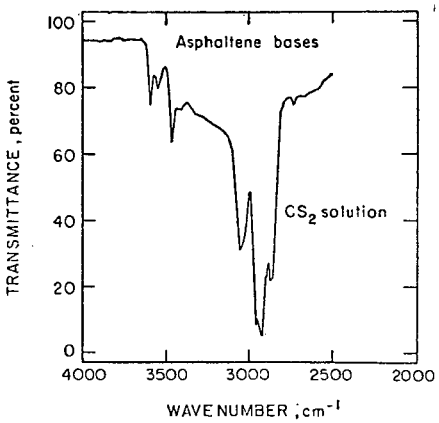

Figure 4. Infrared spectrum of asphaltene bases

TMS derivative and observing the disappearance of the OH bands at 3560 cm-1. The exact nature of these hydroxyls is in question.

Sternberg, et al.(11) stated that they could not detect phenolic OH in the base fraction after TLC and TLE analyses. The base component of Brown, et al. (15) was also tested by TLC and spray reagents and a strong confirmation of phenolic OH was not detected. It is possible that these OH are not phenolic, but more alcoholic in nature, therefore, a positive phenolic test was not observed. Another possibility is that the OH are so hindered that the phenolic reagent could not form its derivative. It is no wonder that many more interesting questions are being proposed than are being answered.

Nuclear magnetic resonance (NMR) has been used to a much greater extent recently due to the advent of computer processing of the signal for enhanced signal-to-noise ratio. We have used both ^{13}C and ^{1}H NMR to determine aromaticity (16) of coal hydrogenation products as well as asphaltenes. An interesting preliminary set of experiments was made for the use of a stable isotope tracer, ^{2}H-deuterium. (14) Another such experiment was made in an autoclave with fresh coal and an asphaltene-free partially deuterated vehicle oil, run at 450° C and pressurized with nitrogen gas in place of hydrogen. If the resulting new asphaltenes, generated from the fresh coal, were found to contain incorporated deuterium, as evidenced by its ^{2}H NMR resonance being greater than natural abundance, then a deuterium transfer could possibly have taken place between the vehicle oil and the coal. Our initial results indicate a slight uptake of deuterium, with some specificity at the aliphatic carbon positions. Work in this area, using stable isotope labels, is continuing and should provide some needed insight into the mechanism of hydrogen transfer in coal liquefaction.

SUMMARY

Over the past 40 years of coal liquefaction, a product that is benzene soluble and n-pentane insoluble, now referred to as asphaltenes, has provided some very interesting questions. We have only touched upon a few of the highlights in the history, isolation, and characterization of these asphaltenes in this presentation. What then is an asphaltene is still an unanswered question. We have yet to establish a standard asphaltene isolation method, hence, only generalization can be made about the final product. Asphaltenes and preasphaltenes might well be the smallest units into which coal may be divided and yet still retain most of the spectral and some of the chemical properties of the original whole coal.

It is therefore not so surprising that we cannot answer the question -

"What are asphaltenes?" .....at this time.

REFERENCES

1. Technical Oil Mission, Reel #7, Library of Congress.

2. M. Pelipetz, E. M. Kuhn, S. Friedman, and H. H. Storch, Ind. Eng. Chem., 40, 1259 (1948).

3. M. G. Pelipetz, S. Weller and E. L. Clark, Fuel, 29, 208 (1950).

4. S. Weller, M. G. Pelipetz, and S. Friedman, Ind. Eng. Chem., 43, 1575 (1951).

5. H. Schultz, M. Mima, and W. McKinstry, private communication.

6. H. W. Sternberg, R. Raymond and F. K. Schweighardt, "Nature of Coal Liquefaction Products," paper presented at Symposium on Progress in Processing Synthetic Crudes and Residues, Division of Petroleum Chemistry, Inc. American Chemical Society, Chicago, August 24-29, 1975.

7. H. W. Sternberg, R. Raymond, and S. Akhtar, "SYNTHOIL Process and Product Analyses", Symposium on Hydrocracking and Hydrotreating, ACS, Philadelphia, April 6-11, 1975. Preprints, Division of Petroleum Chemistry, Inc., ACS, 20, No. 3, 711 (1975).

8. B. Liebenberg and H. G. Potgieter, Fuel, 52, 130 (1973).

9. L. K. Markov and D. B. Orechkin, Trudy Vostochno-Sibir, Filiala, Akad. Nauk. S.S.S.R., 18, 64 (1959).

10. Toluene may be substituted for benzene in consideration of the health hazard associated with benzene vapors. No significant differences have been observed in the final yields.

11. H. W. Sternberg, R. Raymond and F. K. Schweighardt, Science, 188, 49 (1975).

12. R. Husak and C. Golumbic, J. Am. Chem. Soc., 73, 1547 (1951).

13. F. K. Schweighardt, H. L. Retcofsky and R. A. Friedel, Applied Spectroscopy, in press.

14. S. Friedman, C. Zahn, M. Kaufman and I. Wender, Fuel, 40, 38 (1961).

15. F. R. Brown, L. E. Makovsky, S. Friedman and F. K. Schweighardt, Applied Spectroscopy, in press.

16. H. L. Retcofsky, F. K. Schweighardt and M. R. Hough, manuscript in preparation.

17. F. K. Schweighardt, B. C. Bockrath, R. A. Friedel and H. L. Retcofsky, Anal. Chem., in press.

SOLVENT REFINED LIGNITE AND SOLVENT REFINED COAL STRUCTURAL FEATURES. COMPUTERIZED METHODOLOGY DEVELOPMENT.

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Introduction

Recent emphasis on the development of new energy sources has led to increased interest in hydrotreating of coals.[1] Treatment of coals at high temperature and pressure with hydrogen or water and carbon monoxide or both in certain vehicle solvents results in the partial "depolymerization" and reduction of coal.[2] The resulting products, solvent refined coals (SRC), which are freed of solvent and ash by coupled filtration or extraction processes, have lower molecular weights, higher hydrogen and BTU contents, less sulfur and in general greater solubility in solvents. These properties make SRC's desirable boiler fuels as well as reactants for further hydrogenation to premium liquid fuels and chemical feedstocks.

As part of our overall interest in lignite, we have begun a structural investigation of solvent refined low rank coal; lignite or SRL. SRL has properties similar to SRC. SRC's and SRL's cannot readily be structurally investigated by the powerful gas chromatography - mass spectral methods because of their non-volatile nature. Therefore, we have sought alternative general methods for characterizing soluble but non-volatile samples such as SRC and SRL. This communication describes experimental techniques, results, and a computerized modeling method for the chemical characterization of non-volatile coal derived materials.

Because SRL and SRC are soluble in many solvents, a wide variety of analytical techniques can be applied to these samples which are not available for the study of insoluble mixtures like coal itself. These techniques include: nmr, solution ir, and uv spectroscopy, molecular weight determination, and non-aqueous titration. In our work the data obtained by these measurements are correlated by means of a computerized modeling technique to give a better understanding of the average structural and functional group makeup of SRL. We hope that eventually the method will develop into a rapid procedure for gross characterization of organic moieties in SRL and SRC, without the necessity of tedious separation procedures (or at least minimize the separations needed).

Results

The analytical data for SRL's prepared from a number of different refining or vehicle solvents are given in Table 1. Although our focus is on SRL analyses, SRC samples from both bituminous and lignite coals are included in Table 1 for comparison. As can be seen by comparing the analytical data for lignite, an increase in carbon and hydrogen content of SRL over lignite with a corresponding decrease in oxygen and ash is apparent. The same holds true for SRC vs bituminous coal.

The oxygen and nitrogen functionalities are important to further upgrading of SRL. The latter element is a well-known catalyst poison.[3] Consequently, the acidity and basicity of SRL were determined by

potentionmetric titrations. The results are summarized in Table 2 and are a function of vehicle solvent to a degree. The acidic and basic titers of the vehicle solvents themselves as well as for SRC are included in Table 2 for comparison. The results of the acid titrations were reasonably reproducible (1% standard deviation on average) and the acidity of SRL prepared from the same solvent and lignite sample (CAO runs 504 and 505) are nearly identical, The general appearance of the titration curves was similar to that of the titration curve of phenol done in the same manner and different from that of a mixture of phenol and benzoic acid. This suggested a very low carboxylic acid content in SRL, which was also the conclusion from IR studies (cf. later discussion).

The titrations for basic groups were not as reproducible (2% standard deviation on average), but precision was considered adequate considering the low content than the SRC. Both the acidity and the basicity of the SRLs paralleled to some degree the oxygen and nitrogen content of the SRL.

With the exception of the run using Exxon HAN there is a rough correlation between the number of acidic and basic groups in the SRLs. The greater the acidity the greater the basicity. Furthermore, a similar correlation between solvent acidity and SRL acidity and between solvent basicity and SRL basicity exists. This implies that part of the acidity and basicity of the SRL is derived from the refining solvent. This is a factor which must be considered in further reaction studies where these functionalities are influential.

For a more detailed examination of one particular SRL sample, the one prepared using chilled anthracene oil (CAO) as the refining solvent was selected because of the relatively large amount available. Two types of this SRL were on hand (cf. Table 1 , footnotes b and d for the source) prepared by different methods from different lignites. In addition these samples were compared to an SRC prepared from bituminous coal. The two SRL samples vary in their properties which are summarized in Table 3. Over all there is more similarity between the three samples than between bituminous and lignite coals. Also included in Table 3 is the data collected for a reduced SRL distillation fraction prepared by catalytic hydrogenation of KC-SRL.

Infrared spectroscopic measurements on the SRL and SRC samples showed the absence of a carboxylic acid band near 1700 cm^{-1}. Mixtures of benzoic acid with a KC-SRL sample showed that as little as 0.1 meq. of benzoic acid per gram of SRL could have been readily detected. The possibility that a carboxylic acid anion absorption might be present under the strong band near 1620 cm^{-1} was eliminated by treating the SRL with concentrated hydrochloric acid followed by drying under nitrogen (to prevent air oxidation). The infrared spectrum was identical with untreated SRL. These results are consistent with the low carboxylic acid content of SRL inferred from titrimetric data and the chemical conditions for its formation.[4] The total acidity of SRL and SRC samples could not have had more the ca 5% contribution from carboxylic acid groups as a maximum. Carboxylic acid absorption was, however, found in the spectra of unprocessed lignite and air oxidized SRL. Interestingly,the ir spectrum of SRL was almost identical to that reported for bituminous coal,[5] but quite different from that of

unprocessed lignite.

The NMR spectrum of SRL in deuterated pyridine showed three broad absorptions centered at δ 1.2, 2.5 and 7.3 ppm. These were assigned to the aliphatic hydrogens (Halip), the aliphatic hydrogens adjacent to aromatic rings (H_α) (and thus deshielded) and the aromatic ring hydrogens (Har), respectively. The ratio of aromatic to aliphatic protons was $0.73^{\pm}$ .02 for 504-SRL but much higher for KC-SRL at $2.15^{\pm}0.07$ and intermediate for SRC at $1.05^{\pm}0.01$. This compares to 0.75 reported for bituminous coal. NMR deuterium exchange studies revealed that 2.5 meq per gram of protons in 504-SRL could be exchanged.

The ultraviolet and visible spectra of both types of SRL indicate a considerable aromatic region absorption below 300 nm and featureless absorption across the visible region decreasing at longer wavelengths. 504-SRL showed only a smoothly decreasing absorption in the 300-400 nm region but KC-SRL had shoulders at 322 and 336 nm. The $E^{1\%}$ at 320 nm was selected as an absorption which should indicate the degree of polyaromatic condensed ring structure and is also given in Table 3 (all polycondensed ring systems absorb at this wavelength whereas benzene does not). The solvent pyridine was selected to insure complete solubility of the SRLs and SRC while allowing satisfactory absorptions studies down to 310 nm. The $E^{1\%}$ for the reduced fraction is also included in Table 3.

The number average molecular weights of the SRLs (504 and KC), SRC and the reduced fraction (Table 3) determined by vapor pressure osmometry in dimethyl formamide are relatively low. The 400 to 700 range for the average molecular weight before reduction makes application of many standard chemical procedures straight forward. These values have rather large precision errors associated with them and a more detailed study of this difficulty is planned. Never-the-less the relative values should be fairly reliable.

The amount of 504-SRL dissolved by an excess of a given solvent (dissolvability) was measured for 39 solvents at room temperature.[6] These data are presented in Table 4. The values reported are averages of two or three determinations (except as noted) in general with good precision. The SRLs derived from different vehicle solvents show different dissolvabilities, although the same relative order was generally followed.[6] This is shown for SRL(CAO), SRL(FS-120), SRL(Fuel Oil No. 5), and KC-SRL in Table 5.

The dissolvabilities, like the acidic and basic titers, apparently reflect some properties of the vehicle solvent, possibly because of residual solvent in the SRL. Fuel Oil No. 5 SRL was much more soluble in both polar and non-polar solvents than 504-SRL probably because of its more aliphatic nature. (Fuel oil is more aliphatic than anthracene oil). 504-SRL is the least soluble in hexane probably reflecting the high aromatic character and higher average molecular weight.

It is quite evident from Tables 1-5 that SRLs derived from different vehicle solvents have somewhat different properties. An SRL prepared from the same lignite with the same vehicle solvent will probably be fairly consistent in properties when prepared by the same procedure (cf. SRL-504 properties).

The fact that the SRL takes on some of the acidic, basic and dissolvability characteristics of the vehicle solvent is understandable. Of course in a commercial process the vehicle solvent will be coal derived. At any rate, these data indicate that the quality as well as the quantity of the coal derived vehicle solvent will be critical.

Utilizing the data presented in Tables 1, 2 and 3 the more informative data in Table 6 may be calculated. The average molecular weight allowed calculation of an average molecular formula, the uv absorbitivity (at 320 nm) and the number of equivalents of acid and base per average molecule.

This analysis can be carried further by inclusion of the nmr data. The method of analysis has been discussed previously by others.[7] The nmr spectrum is separated quantitatively into three areas; the aromatic protons (H_{ar}), the aliphatic protons adjacent to aryl rings (H_{α}) and all other aliphatic protons (H_o). Several assumptions are made in the analysis. First, the average number of hydrogens on carbons attached to aryl rings (X) must be fixed. All calculations were made with this value fixed at X=2.00. This value is close but not correct for every sample. However, the relative value of the parameters calculated appear valid. Secondly, the average number of hydrogens on carbons attached to aryl rings was assumed to be the same as the average number of hydrogens attached to aliphatic carbons away from aryl rings. Furthermore, all the oxygen was assumed to be attached to aryl rings. The phenol hydrogens are known to be under the aryl proton absorption in the nmr so that only non acidic oxygen was used in the calculations (ie. the difference between the moles of oxygen and the moles of phenol per mole of average molecules was used for the oxygen to correct Har). Lastly, the sulfur and nitrogen contents were low and were, therefore, ignored. Using the data and these assumptions it was possible to calculate the following: the average number of aromatic carbons per average molecule (C_a), the average number of aromatic rings per average molecule (R_a), the average number of hydrogens on the average aromatic portions of the average molecule after all substituents have been replaced with hydrogen (H_a), the average number of aromatic edge atoms which are substituted (σ) and the average length of aliphatic side chains attached to the aryl rings ($C\ell$). The details of the calculations are summarized briefly in the Experimental Section.

The purpose of including in the analysis the fraction 59-3, a reduction fraction of KC-SRL boiling at 139-200 C (1 Torr), was to compare the outlined analysis in so far as possible with a detailed mass spectral analysis carried out on this fraction by Gulf Oil Company at our request. The Gulf analysis showed that 59-3 was 100% aromatic, ie. all constituent compounds had an aromatic moiety. The mass spectral type analysis gave the percent composition of the mixture in terms of general types of molecules of aromatic and hydroaromatic structure. From their molecular formula assignments structural assignments were made by assuming for each molecular formula the greatest number of aromatic rings. From the structural assignments and the mole percent of each in the mixture it was possible to obtain the weighted average for C_a, H_a and R_a shown in the first entry of Table 7. Considering the assumptions made in the nmr analysis, the deviations are gratifyingly small. The value of X assumed as 2.00 in the nmr analysis cannot alone explain the deviations from the

ms analysis. Because H_a was derived from C_a it would be reasonable to assume the largest error in H_a rather than in C_a. Calculation of the X necessary to give the same C_a as obtained from the mass spectral analysis gave X = 2.062 (Table 7, entry 3). With this value, however, H_a became lower (7.35), thus increasing the deviation from the ms data value. The values from the nmr analysis can be brought into consistence with the ms values by adjusting X so as to give the same Ha/Ca ratio, then increasing the molecular weight of 59-3 to give the same Ca value (Table 7, entry 4). The molecular weight increase (5.6 or 2.9%) is within experimental error of the VPO method and the X value calculated (1.967) is very close to the original 2.0 value. Thus the two analyses are within experimental error of each other. The differences in C_a and H_a values must, therefore, result from the cumulative errors of both analyses. This ms procedure might be used to fix an X value for use on SRL and SRC samples by analogy; however, carbon-13 nmr offers a more systematic approach to X values and we are examining this possibility further. The value of X = 2.00 assumed for the SRLs and SRC must be near the correct value as the above data shows and does provide a means of comparing the samples.

It is instructive to consider the differences between different solvent refined coals using the data presented in Table 6. By comparing the average molar absorbtivity of each SRL to the average number of aromatic rings present, Ra, it appears probable that the average molecule is not made up of only one polycondensed aromatic moiety. For example, 504-SRL with Ra = 7.94 rings and E_{320} = 32,000 cannot have seven or eight rings polycondensed because most ring systems this size have molar absorbtivities between 50,000 and 150,000 at this wave length. A combination of two or three chromophores of smaller size connected by short chains, however, could explain the observed average values.

It also appears for our samples that from 0.5 to 1.4 equivalents of acidic groups are present per average mole. Because of the lack of carbonyl absorption, this probably means somewhere near one phenolic function per average molecule. The remainder of the oxygen probably is present mainly as ethers. The amount of nitrogen seems well divided between basic and non basic groups probably both aromatic (pyridine and pyrrole like respectively).

Comparison of 504-SRL with KC-SRL.

504-SRL has a higher molecular weight, a higher degree of aryl substitution (Fa) and longer chains as substituents (C_ℓ) than KC-SRL. This accounts for the lower (Har/Hal) ratio for 504-SRL. KC-SRL has smaller molecules which have a higher degree of aromatic character (88% of KC-SRL carbons are aromatic but only 77% of 504-SRL carbons are aromatic, cf.). In addition 504-SRL has more than one equivalent of phenol per molecule while Kc-SRL has slightly more than one half an equivalent per molecule. KC-SRL is also less basic but only slightly (the difference in the number of equivalents per mole is only 0.17).

These differences could arise from the different lignites used in their preparation but for reasons discussed below it seems more reasonable to attribute the differences to the different modes of preparation. The data indicates 504-SRL was prepared under conditions which allowed better

reduction but poorer "depolymerization" than were the conditions for KC-SRL preparation. The latter could also be responsible for the lower acid and base titers of KC-SRL. Greater depolymerization might also means greater deoxygenation, or perhaps this could be caused by greater attack at phenolic rings followed by cleavage, dehydration and reduction.

Comparison of SRLs to SRC.

A similar detailed comparison of SRC with the SRLs is very interesting. Nearly all critical comparisons put SRC close to or between the values of the two SRLs. Only the molar absorbtivity and the number of equivalents of base permole are marginally outside the values of the SRLs. These facts indicate a general insensitivity of properties of the products to the general mode of preparation and the source of coal. Both lignite and bituminous coals give solvent refined products which are more similar to each other than are the starting coals. Care must be exercised, however, in concluding the general similarity or divergence of properties of SRC vs. SRL from our limited data due to storage times and sample preparation differences.

We feel the conclusions drawn about the relative properties of these particular samples are valid. It must be remembered, however, that these samples are probably not representative of what will be produced by plant or pilot plant operation but represent samples and experimental procedures which we had available to develop our comparisons. A much more systematic investigation of the dependence of solvent refined coal properties on liquefaction conditions and coal source may or may not verify the preliminary indications we report here.

The comparison, however, can be made reasonably well with readily available analyses, without tedious separations. Analytical accuracy and precision are at present either undefined or too high and we are attempting to realistically assess the errors inherent in the assumptions by more detailed separations and determinations and by different analyses.

Projections

Because of interest expressed privately in our projected computer modeling study, it seems worth while to outline the approach we are taking in this analysis and to point out some of the problems.

Any molecular property of the mixture which can be expressed as the sum of the properties of the constituent compounds in the mixture can be used to set up an equation expressing this relationship. For example, the average molecular weight of a mixture is the weighted average of the molecular weights of the constituent compounds:

$$C_1X_1 + C_2X_2 + C_3X_3 + \cdots\cdots C_nX_n = X_{mix}$$

C_i = mole fraction of i

X_i = molecular weight of i

We do not know the molecular formula for the constituent compounds in the mixture of a SRL. The properties calculated previously, however, are known and can be related to the properties of the mixture. Thus, a series of equations containing C_a, H_a, basic and acidic titers and the ultraviolet spectral data can be set up in terms of the aromatic portion of the constituent molecules. For example, phenanthrene has $C_a = H_a = 10$, acid and base titers of 0.0 with the ultraviolet spectrum extracted from the literature using the molar absorbtivity at as many wavelengths as desirable. With this data for a wide selection of compounds, a series of linear equations can be set up in a matrix form which will describe the general properties of the mixture in terms of the properties of the aromatic (neutral, basic and acidic) moieties of the constituent compounds. In principle a matrix of this sort can be solved exactly to give the mole fraction of each aromatic component. In practice, the method of matrix solution is apparently critical as is the particular basis set of possible constituent compounds which are selected. Methods of matrix solution which allow impostion of limits for certain component mole fractions (eg. determined by separation procedures, etc.) and methods allowing estimation of errors are currently being investigated. Furthermore, the effect of the partial redundancy of the data must be investigated in detail to provide the best basis set of aromatic compounds. We hope to be able to describe the details of this approach in the near future.

Experimental Section

General.

Analyses were performed in the Chemical Engineering or Chemistry Departments of the University of North Dakota using 0.05 to 0.5 g samples. Sulfur analysis was performed using a Leco apparatus; nitrogen by a Keidahl procedure. Molecular weights were determined by Spang Microanalytical Laboratory in dimethylformamide by vapor pressure osmometry. Infrared spectra were determined on a Beckman 1R-12. NMR spectra were determined on a Varian A-60.

Dissolvability Studies

A sample of solvent refined coal or lignite (0.15±0.2 g) in 30 ml of the solvent was stirred with a magnetic stirring bar at room temperature (20-25°C) for 30 min. and then filtered. The filtrate was first evaporated to dryness in a rotary evaporator then evacuated with a vacuum pump for 30 min more and weighed. Partially dissolved samples were generally run in duplicate or triplicate with the percentage standard deviations of 1-4% for class 2 solvents and 1-18% for class solvents reported in Table 4.

Titrations. A. Determination of Basic Content.

The amount of basic nitrogen in SRL or SRC was determined by titration of a sample ($\leq$0.3g) dissolved in 50 ml of nitrobenzene and 5 ml of glacial acetic acid with 0.1 M perchloric acid in dioxane solution. The end point was determined potentiometrically using a pH meter equipped with a calomel and a standard glass electrodes. Duplicate or triplicate titrations gave the data in Table 2. Standard deviations ranged from 0.1% to 2.5%, with an

average of 1%.

b. Determination of Acid Content.

The amount of acids (phenols) in SRL and SRC were also determined by nonaqueous potentiometric titration. A sample (<0.3g) was dissolved in 50 ml of pyridine and titrated under a nitrogen atmosphere with 0.1 M tetrabutyl ammonium hydroxide in dry benzene solution. The potentiometric end point was determined with a pH meter coupled to a standard glass electrode and a modified calomel electrode having a sleeve type electrode. The calomel electrode was modified by substituting anhydrous methanol for water in the salt bridge. Duplicate or triplicate runs gave the data in Table 2. Standard deviations ranged from 0.5 to 5.4% with an average of 2%.

NMR Analysis

Brown Ladner's Aromaticity Equations.

This procedure defines three parameters in terms of the percent composition (carbon, hydrogen and oxygen only) and the nmr spectrum:

Fa, σ , Ha/Ca

$$Fa = \frac{C_{\tau}/H_{\tau} - \left(\frac{H\alpha^*}{x} + \frac{Ho^*}{y}\right)}{C\tau / H\tau}$$

$$\sigma = \frac{\left(\frac{H\alpha^*}{x} + \frac{O\tau}{H\tau}\right)}{Har^* + \frac{H\alpha^*}{x} + \frac{O\tau - Oa}{H\tau}}$$

$$C\ell = \frac{H\alpha^* + Ho}{H\alpha}$$

$$\frac{Ha}{Ca} = \frac{\frac{H\alpha^*}{x} + Har^* + \frac{O\tau - Oa}{H\tau}}{Fa\,\frac{C\tau}{H\tau}}$$

$$Ra = \frac{Ca - Ced}{2} + 1$$

Where:

$C\tau$= mole % carbon

$H\tau$= mole % Hydrogen

$O\tau$= mole % oxygen

O_a= mole % acidic oxygen

$H\alpha^* = \frac{H\alpha}{H_N}$ = molar ratio of hydrogen α to aryl ring to total Hydrogen present from nmr

$Ho^* = \frac{Ho}{H_N}$ = molar ratio of aliphatic hydrogen not α to aryl ring to total hydrogen present from nmr.

x = average ratio of hydrogen to carbon on carbons α to aryl ring

y = average ratio of hydrogen to carbon on alphatic carbons not α to aryl ring

Fa = the fraction of total carbon present that is aromatic carbon = $\frac{Ca}{C\tau}$

σ = the average number of available aromatic edge atoms which are substituted by aliphatic carbons. $\frac{C\alpha}{Ced} = \frac{C\alpha}{Ha}$

$\frac{Ha}{Ca}$ = ratio of substitutable edge atoms to total aromatic carbon.

C_ℓ = average aliphatic chain length

Ra = average ring size

Assumptions:

All oxygen is attached to aryl rings (ie phenolic or aryl ether).

Phenolic hydrogens are under aryl absorption in nmr

NMR of Ar-O-$\underline{CH}_2$ protons under Hα absorptions

That x = y = 2.00.

The equations presented above are a slight modification of the originals to compensate for the measured acidity of the SRC samples.

Procedure:

NMR: the nmr spectrum is divided into aryl (δ<6.5 ppm), Hα (3.5 - 5.5 ppm) and Ho (0.5 - 3.5 ppm) regions from which Ha^*, Ho^* and $H\alpha^*$ can be calculated. The values reported are the average of four to six integrations at a low rf field to prevent saturation effects. The nmr spectrum was run in perdeutero pyridine using octamethylcyclotetrasiloxane as standard. The ratio of residual pyridine proton absorptions to the standard absorption was calibrated prior to dissolving the sample and subtracted away from Har of the sample integral. The low volatility of the standard facilitated reproducible pyridine: standard ratios.

References

1. A. M. Squires, Science, 191, 690 (1976).
2. H. Appell, I. Wender, and R. D. Miller, Amer. Chem. Soc. Fuel Div. Preprints, 13 (4), 39 (1969).
3. C. L. Thomas, "Catalytic Process and Proven Catalysts", Academic Press, N. Y., 1970, p. 158.
4. K. D. Bartle, T. G. Martin and D. F. Williams, Fuel, 54, 226 (1975).
5. Results from Project Lignite, Dept. of Chemical Engineering, University of North Dakota, Grand Forks, N. D. 58202.
6. Solubility is different from dissolvability. The latter is measured under equilibrium conditions but the dissolved solute is a mixture and probably has a different composition than the undissolved solute which is also a mixture. Thus, dissolvability is really a measure of the percentage of soluble material in that particular solvent for a given coal derived sample.
7. J. K. Brown and W. R. Ladner, Fuel, 39, 87 (1960). (For a recent application see G. A. Haley, Anal. Chem. 43, 371 (1971) and D. R. Clutter, L. Petrakis, R. L. Stenger, Jr., and R. K. Jensen, ibid., 44, 1395 (1972).

Table I

Analytical Data[a] for SRLs from

Different Refining Solvents

Wt%

SRL[b]	C	H	N	S	O	Ash
504 CAO[c]	85.57	5.62	1.83	0.30	6.57	0.11
504 CAO[c]	88.06	5.60	1.70±.23	0.26	4.38	
KC CAO[d]	89.14	5.46	1.46	0.52	3.18	0.24
FS 120[e]	89.27	5.81	0.85±.025	0.96	2.98	0.13
Tar S2[f]	90.10	5.79	0.68	0.60	2.77	0.06
Fuel Oil #5[g]	87.63	8.74	1.01	1.34	1.20	0.08
Exxon HAN[h]	86.93	7.01	1.84	0.24	3.98	
SRC-88-18[i]	87.55	5.38	2.11	0.68	4.21	0.07
N. D. Lignite	60-65	4-4.5	0.5-1	0.7-1.0	20	6-7.5
Bituminous Coal[j]	70-90	4.5-5.5	1.0-1.5	1.0-2.0	5-20	1-2
59-3[k]	90.62	8.35	0.53	0.19	0.05	

a. Analytical data determined by Project Lignite (except SRC-88 and KC-SRL) on a moisture free basis.

b. These samples were prepared by Project Lignite in batch autoclave studies; runs 504 and 505 were duplicate runs (conditions: initially 1000 psi of 1:1 H_2CO at room temperature then heated to 400° C. for 30 min.; filter at 200° C. SRL is vacuum bottoms from distillation to 255-270° @ 1.6 Torr).

c. Chilled anthracene oil, CAO, ibp 234, 3% 234-269°C; 22%, 269-314°C; 36% 314-354°C; 38.3% 354-residue.

d. Sample prepared in a laboratory continuous flow apparatus by Spencer Chemical Co. (now Pittsburgh and Midway Coal Co. a subsidiary of Gulf Oil Co.) Kansas City

e. FS - 120: a petroleum feedstock, ibp. 316°C, 97% less than 354°C at atmospheric pressure.

f. Tar S2: bottoms from steam cracking petroleum residues at atmospheric pressure, ibp. 271° C; 21% at 268-313°C; 24% at 313-353° C; 55% at 353 353[8] residue.

g. Fuel Oil Number 5: ibp. 276°C; 0.5% 268-313; 3% 313-353°; 96% 353 residue.

h. Exxon HAN, ibp 214°C; 9% 209-234°; 70% 234-269°; 19% 269-314°;1% 314-354°; 0.5% 354° residue.

i. SRC-88-18: a solvent refined coal prepared by Pittsburgh and Midway Coal Co. in a continuous flow apparatus. (conditions: coal, Kentucky #9 and #14 blend bituminous in a 33% slurry with a partially hydrogenated anthracene oil; temperature 425-450; hydrogen pressure of 1500 psi; feed rate 520 g/hr.)

j. W. A. Bone and G. W. Himus, "Coal, Its Constitution and Uses", Lengmuns, Green and Co.,N. Y., 1936. Chap. 4 and 5.

k. KC-SRL reduction fraction

l. The oxygen and nitrogen analyses courtesy of DuPont de Nemoirs Co.

Table 2

Refining Solvent[a]	Acid Titer (meq/g)		Base Titer (meq/g)	
	SRL	Solvent	SRL	Solvent
SRL				
504 CAO	2.18	0.453	0.614	0.403
505 CAO	2.10	NA	0.629	NA
KC CAO	1.34	NA	0.535	NA
FS 120	1.53	0.032	0.300	0.024
Tar S2	1.49	0.196	0.288	0.022
Fuel Oil #5	0.69	0.090	0.161	0.0056
Exxon HAN	2.48	0.007	0.452	0.008
SRC-88	2.15	NA	0.82	NA

a. of Footnotes Table 1 cf

Table 3

Property	Sample			
	59-3	504-SRL	KC-SRL	SRC-88
MW	195	620	400 ± 40	563 ± 34
UV $E^{1\%}_{320}$	77	514	494	580
Har/Halip	0.459	0.729	2.250	1.066

Table 4

Dissolvability of Organic Solvents

for 504 SRL

Solvent	% Dissolved
Class 1	
Nitromethane	6.3
Pentane	6.9
Heptane	7.9
Hexane	11.7
Carbon tetrachloride	20.2
Formic Acid	25.3
Methanol	32.4

Table 4 (cont.)

Solvent	% Dissolved
Class 2	
Acetic Acid	47.1
Ethanol	47.2
1-Propanol	50.8
1-Butanol	52.0
Mesitylene	52.6
Diethyl ether	54.6
Toluene	58.2
Propanoic Acid	59.5
Butoanoic Acid	59.3
Benzene	62.0
Phenyl acetate	67.0
Acetone	69.8
Dichloromethane	69.8
1-Nitropropane	70.0
Nitroethane	70.4
Chloroform	75.7
Anisole	77.1
Butanone	80.5
Ethylacetate	84.0

Table 4 (cont.)

Solvent	% Dissolved
Class 3	
Methyl benzoate (trace left)	CA 100
Dioxane (trace left)	CA 100
Acetophenone	100
Tetrahydrofuran [b]	100
Pyridine	100
Nitrobenzene	100
Phenol	100
Dimethyl sulfoxide	100
Dimethyl formamide	100
n-Hexylamine	100
n-Butylamine (trace left)	CA 100
Dimethyl aniline	100
Aniline	100

a. Single determination

b. The same SRL from different containers have given varying solubilities in this solvent. Solvent purity also has some effect.

Table 5

Dissolvabilities of SRLs

	504	KC	FS-120	Fuel Oil No. 5
Pyridine	100	100	100	100
Phenol	100	NA	100	100
Nitrobenzene	100	100	100	100
n-Butylamine	100	100	100	100
Benzene	61.9	62.2	67.6	100
n-Butanol	52	NA	63.5	91.3
95% Ethanol	47.0	42.2	NA	51.5
Methanol	32.4	40.2	34.0	34.3
Propanol	50.8	NA	NA	86.6
Amyl Alcohol	NA	NA	NA	96.8
Hexane	11.6	NA	NA	73.6

Table 6

Average Molar Properties

	59-3	504-SRL	KC-SRL	SRC-88
Molecular formula	$C_{14.75}H_{16.20}$ $S_{0.01}N_{0.07}O_{0.01}$	$C_{44.22}H_{34.62}$ $S_{0.06}N_{0.81}O_{2.55}$	$C_{29.76}H_{21.71}$ $S_{0.06}N_{0.42}O_{6.80}$	$C_{41.07}H_{30.05}$ $S_{0.12}N_{0.85}O_{1.48}$
Base eq/mole	NA	0.381	0.214	0.46
Acid eq/mole	NA	1.35	0.536	1.21
Non acidic O	NA	1.20	0.264	0.27
Non basic N	NA	0.43	0.20	0.39
ROH	NA	0.20	NA	NA
E (320nm)	1500	31,900	19,800	32,700
NMR Data				
Fa	0.624	0.774	0.884	0.823
σ	0.313	0.305	0.177	0.308
Ha/Ca	0.806	0.558	0.658	0.612
Ca	9.201	34.20	26.29	33.80
Ha	7.417	19.07	17.31	20.67
Ra	1.897	8.57	5.49	7.56
C_ℓ	2.39	2.24	1.37	1.41

Table 7

Comparison of MS and NMR Data

	X	Fa	Ha/Ca	Ca	Ha	Ra
Ms Data	___	0.635	0.819	9.368	7.673	1.848 (1.857)
NMR Analysis						
Mw = 195	2.0	0.624	0.806	9.201	7.417	1.892
Mw = 195	2.06	0.635	0.784	9.368	7.348	2.01
MW = 195	1.97	0.617	0.819	9.096	7.450	1.823
MW = 200.6	1.97	0.617	0.819	9.37	7.67	1.848