

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.<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup> Consequently, the acidity and basicity of SRL were determined by

potentiometric 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  $1700\text{ cm}^{-1}$ . 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  $1620\text{ cm}^{-1}$  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.<sup>4</sup> The total acidity of SRL and SRC samples could not have had more than 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,<sup>5</sup> but quite different from that of

unprocessed lignite.

The NMR spectrum of SRL in deuterated pyridine showed three broad absorptions centered at  $\delta$  1.2, 2.5 and 7.3 ppm. These were assigned to the aliphatic hydrogens (Halip), the aliphatic hydrogens adjacent to aromatic rings ( $H_a$ ) (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  $E_{1\%}^{1\text{cm}}$  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  $E_{1\%}^{1\text{cm}}$  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.<sup>6</sup> 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.<sup>6</sup> 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.<sup>7</sup> The nmr spectrum is separated quantitatively into three areas; the aromatic protons ( $H_{ar}$ ), the aliphatic protons adjacent to aryl rings ( $H_{\alpha}$ ) and all other aliphatic protons ( $H$ ). 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  $H_{ar}$ ). 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 ( $\sigma$ ) 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  $C_a$ ,  $H$  and  $R$  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,  $R_a$ , it appears probable that the average molecule is not made up of only one polycondensed aromatic moiety. For example, 504-SRL with  $R_a = 7.94$  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 ( $F_a$ ) and longer chains as substituents ( $C_\ell$ ) 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 mean 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 absorptivity 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:

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

$C_i$  = 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 imposition 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 Keldahl procedure. Molecular weights were determined by Spang Microanalytical Laboratory in dimethylformamide by vapor pressure osmometry. Infrared spectra were determined on a Beckman IR-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.

##### Titration. A. Determination of Basic Content.

The amount of basic nitrogen in SRL or SRC was determined by titration of a sample (<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,  $\sigma$ , Ha/Ca

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

$$\sigma = \frac{(H\alpha^* + O_{\tau})}{x + H_{\tau}}$$

$$Ha\tau^* + \frac{H\alpha^*}{x} + \frac{O_{\tau} - O_a}{H_{\tau}}$$

$$Ce = \frac{H\alpha^* + H\alpha}{H_{\alpha}}$$

$$\frac{Ha}{Ca} = \frac{H\alpha^* + Ha\tau^* + \frac{O_{\tau} - O_a}{H_{\tau}}}{\frac{Fa C_{\tau}}{H_{\tau}}}$$

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

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  $\alpha$  to aryl ring to total Hydrogen present from nmr

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

x = average ratio of hydrogen to carbon on carbons  $\alpha$  to aryl ring

y = average ratio of hydrogen to carbon on aliphatic carbons not  $\alpha$  to aryl ring

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

$\sigma$  = the average number of available aromatic edge atoms which are substituted by aliphatic carbons.  $\frac{Ca}{C_{ed}} = \frac{Ca}{Ha}$

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

$C_2$  = 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-CH<sub>2</sub> protons under Ha 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 ( $\delta < 6.5$  ppm), Ha (3.5 - 5.5 ppm) and Ho (0.5 - 3.5 ppm) regions from which Ha\*, Ho\* and H<sub>N</sub> 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 Ha<sub>r</sub> 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 1  
Analytical Data<sup>a</sup> for SRLs from  
Different Refining Solvents

<u>SRL</u> <sup>b</sup>	<u>Wt%</u>					
	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>O</u>	<u>Ash</u>
504 CAO <sup>c</sup>	85.57	5.62	1.83	0.30	6.57	0.11
504 CAO <sup>c</sup>	88.06	5.60	1.70 <sup>±.23</sup>	0.26	4.38	
KC CAO <sup>d</sup>	89.14	5.46	1.46	0.52	3.18	0.24
FS 120 <sup>e</sup>	89.27	5.81	0.85 <sup>±.025</sup>	0.96	2.98	0.13
Tar S2 <sup>f</sup>	90.10	5.79	0.68	0.60	2.77	0.06
Fuel Oil #5 <sup>g</sup>	87.63	8.74	1.01	1.34	1.20	0.08
Exxon HAN <sup>h</sup>	86.93	7.01	1.84	0.24	3.98	
SRC-88-18 <sup>i</sup>	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 <sup>j</sup>	70-90	4.5-5.5	1.0-1.5	1.0-2.0	5-20	1-2
59-3 <sup>k</sup>	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<sub>2</sub>CO 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<sup>8</sup> 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 Nemours Co.

Table 2

Refining Solvent <sup>a</sup>	<u>Acid Titer (meq/g)</u>		<u>Base Titer (meq/g)</u>	
	SRL	Solvent	SRL	Solvent
<u>SRL</u>				
504 CA0	2.18	0.453	0.614	0.403
505 CA0	2.10	NA	0.629	NA
KC CA0	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

<u>Property</u>	<u>Sample</u>			
	<u>59-3</u>	<u>504-SRL</u>	<u>KC-SRL</u>	<u>SRC-88</u>
MW	195	620	400 <sup>±</sup> 40	563 <sup>±</sup> 34
UV E <sub>320</sub> <sup>1%</sup>	77	514	494	580
Har/Halip	0.459	0.729	2.250	1.066

Table 4  
Dissolvability of Organic Solvents  
for 504 SRL

Solvent	<u>Class 1</u>	% Dissolved
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	<u>Class 2</u>	% Dissolved
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
Butanoic 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
<u>Class 3</u>	
Methyl benzoate (trace left)	CA 100
Dioxane (trace left)	CA 100
Acetophenone	100
Tetrahydrofuran <sup>b</sup>	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

	<u>504</u>	<u>KC</u>	<u>FS-120</u>	<u>Fuel Oil No. 5</u>
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 <sub>14</sub> H <sub>16</sub> O <sub>2</sub> S <sub>0.01</sub> N <sub>0.07</sub> O <sub>0.01</sub>	C <sub>44.22</sub> H <sub>34.62</sub> S <sub>0.06</sub> N <sub>0.81</sub> O <sub>2.55</sub>	C <sub>29.76</sub> H <sub>21.71</sub> S <sub>0.06</sub> N <sub>0.42</sub> O <sub>1.80</sub>	C <sub>41.07</sub> H <sub>30.05</sub> S <sub>0.12</sub> N <sub>0.85</sub> O <sub>1.48</sub>
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
<u>NMR Data</u>				
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 <sub>g</sub>	2.39	2.24	1.37	1.41

Table 7  
Comparison of MS and NMR Data

	<u>X</u>	<u>Fa</u>	<u>Ha/Ca</u>	<u>Ca</u>	<u>Ha</u>	<u>Ra</u>
Ms Data	_____	0.635	0.819	9.368	7.673	1.848 (1.857)
<u>NMR Analysis</u>						
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