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DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES TO CHEMISTRY OF DONOR SOLVENT LIQUEFACTION

Final Report, August 31, 1977–December 31, 1979

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FINAL REPORT

The scope of this project was to develop and apply analytical techniques for the characterization of coal conversion products. Solvent refined coal served as the coal derived material for the duration of the study. The investigation has been focused primarily in the areas of separations and nuclear magnetic resonance spectroscopy. Highlights of the twenty-eight month study are listed below followed by a brief synopsis of our major findings.

I. SEPARATIONS

- A. Size Exclusion Chromatography of SRC Models
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I-A. Size Exclusion Chromatography of SRC Models

A major obstacle in characterizing a product of donor solvent coal liquefaction is separation of the material into fractions each of which can be described in relatively simple terms. In general, two approaches have emerged so far in dealing with this problem: (1) a broad but rather crude separation of approximately all of the coaly matter, and (2) a much "finer" separation of only a relatively small percentage of the total coaly product. Our emphasis to date has been concerned with the former. Separation via size offers a number of advantages in this regard. Single operation procedures and near complete recovery of material are two very attractive features. Since the functionality and nature of the coal liquid are exceedingly complex we have performed a GPC model compound study to determine the elution patterns for a variety of organic functionalities. The packing material employed has been Bio Beads S series. This soft gel is attractive for coal liquids separation because precipitation arising from intermolecular association occurs during the separation which naturally precludes the more efficient, more expensive GPC rigid and semi-rigid packings. Bio Beads have not been as extensively investigated as their harder, diluent-controlled pore size counterparts.

Plots of log molecular weight vs retention volume for n-alkanes on Bio Beads SX-2, SX-4, SX-8, and SX-12 in THF were made. Propane

appears in the totally permeated region. Hydrocarbons up to $n\text{-C}_{40}\text{H}_{82}$ fall in the selectively permeated region. Insolubility of higher n -alkanes in THF dictated the employment of polystyrene standards in order to find the totally excluded molecular weight. Higher percent crosslinking gave rise to lower exclusion limits (for SX-2, SX-4, SX-8, and SX-12 the excluded molecular weights are 1700, 850, 510, and 320, respectively, based on n -alkanes).

Plots of $\log MW$ versus K_d were established for acids, alcohols and diamines. As can be seen in Figure 1, as an example, no homologous series coincides with the alkanes. Both the alcohol and carboxylic acid series appear to approach asymptotically to the alkane curve. The alkyl diamines lay above the alkane curve in contrast to the acids and alcohols which lay below the alkane curve. This would imply that the solvated diamine species appear to be smaller than the same molecular weight alkane, whereas, the alcohols are larger than the alkanes but smaller than the acids. One may rationalize this observation strictly as a moiety size effect where the order from small to large is $-\text{NH}_2 < -\text{CH}_2- < -\text{OH} < -\underset{\text{O}}{\underset{||}{\text{C}}}-\text{OH}$ or as a solvent/solute interaction effect.

The elution pattern for several other series of related compounds has been investigated. A plot of $\log MW$ versus K_d for alkyl benzene from benzene to n -butyl benzene is linear for SX-4, -8, and -12 and corresponds to the selective permeation region. A similar plot of fused aromatic six-membered ring systems is also obtained. The straight line plot for these materials exhibits a much steeper slope than the plot for n -alkanes suggesting that

Figure 1

the separation of n-alkanes would be superior to the separation of fused-ring aromatics on Bio Beads. Additional aromatic materials (e.g. biphenyl and binaphthyl) and several cyclic aliphatic systems (e.g. cyclohexane, norbornane and cholestane) have been investigated. The behavior of cyclic aliphatics was similar to n-alkanes, whereas the behavior of compounds such as biphenyl and binaphthyl mimicked the fused-ring aromatics. Plots of various homologous series yield slopes in the selective permeation region which are quite different. This is best illustrated by N-substituted anilines which yield a positive rather than a negative slope. The differences in slope, we believe, are indicative of a sorption phenomenon in addition to size exclusion. It is interesting to compare the aniline family (e.g. aniline to N,N,N',N'-tetramethyl-p-phenylenediamine) with benzene substituted aliphatic amines such as mono-, di- and tri-benzyl amines. Why the latter should exhibit size exclusion and the former adsorption with Bio Beads is unknown. For comparison purposes, ring nitrogen-containing systems (carbazole, pyridine, etc.) behave as the hydrocarbon fused-ring materials discussed earlier.

Clearly enormous difficulties can arise in interpreting the chromatogram of a complex mixture based on a single calibration curve. Only in cases where the components come from a single homologous series could this approach be failsafe. A dramatization of this problem is demonstrated in the separation of a synthetic

mixture composed of dodecane (180), aniline (93), and anthracene (178). Exhibiting practically baseline separation, aniline, with half the molecular weight of the other two, lies between dodecane and anthracene. Better than baseline separation is observed for dodecane and anthracene although the two differ by only 2% in molecular weight.

The employment of THF as the solvent in size exclusion chromatography is extensive. For separating coaly matter THF does not always prove satisfactory because the THF undergoes decomposition under numerous conditions in the presence of SRC. For this reason the interaction of Bio Beads with chloroform and pyridine and the separation of various homologous series in these solvents were investigated. Exclusion limits for Bio Beads SX-4 in the three solvents with n-alkanes were obtained. It is interesting to note that plots of CHCl_3 and THF data nearly overlap while the pyridine results are clearly displaced. Interpretation of this result indicates that in pyridine the same alkane exhibits a smaller effective molecular size than in either of the other two solvents. This observation implies a higher apparent exclusion limit in pyridine (1750) relative to THF (950) and CHCl_3 (900). One rationale for this behavior is that the more solvated the species the more extended (or larger) it should appear. Pyridine should not solvate alkanes as well as THF or CHCl_3 . The alternative explanation involving solvent-gel interaction is negated by the fact that the gels swell more in CHCl_3 than in THF or pyridine.

A comparison of carboxylic acids, diamines and alkanes on an SX-4 column with pyridine as the solvent reveals that the acids appear larger than the alkanes as in THF, but in contrast to THF the diamines also appear larger.

I-B. Size Exclusion Chromatography of SRC

A preparative quantitative separation of THF- and CHCl_3 -soluble solvent refined coal (Pittsburgh No. 8) has been demonstrated employing gel permeation chromatographic techniques utilizing a styrene-divinyl benzene packing (Bio Beads S-X4). In an attempt to introduce and separate larger amounts of SRC solid product, numerous glass column designs were studied. Glass was employed in that it offered several advantages such as easier column fabrication, a readily observed separation, and fewer contamination problems. The column design which proved to be most suitable for our purposes was 37 mm in diameter and 100 mm in length with a 60 mm taper.

Injections were normally made with a 50% THF saturated solution. Injections of more dilute solution did not alter the parameters of the separation. The column overload point was ~ 1.5 g/15 mL injection. Beyond a 1.5-g load, the chromatogram began to lose resolution. The HETP was determined on the Bio Bead S-X4 column and found to be 1024 TP/foot. Total accessible ($V_T=92\text{mL}$) and excluded ($V_0=35\text{mL}$) volumes were estimated from the raw chromatograms since the nature of the molecules of the coal

liquid is not established. A comparison with an empty column volume of approximately 150 mL suggests a normal GPC separation mechanism.

In an effort to establish, in fact, if a separation based on size had occurred with Bio Beads S-X4, average molecular weights on the four fractions taken were necessary. Since our separation involved gram quantities, molecular weights of each fraction evaporated to dryness and redissolved in THF were determined in duplicate by vapor phase osmometry. The highest molecular weight components appear to be eluted from the column first as would be expected. Later fractions have lower average molecular weights suggesting a separation based generally on molecular weight. One must be cautioned here, however, since the numbers quoted are number average molecular weights and these data will only equal the weight average molecular weight if the weight range of molecules in each fraction is relatively small and/or the distribution of molecular weights is fairly uniform.

The amount of material recoverable from the column in a preparative size-separation is critical. By injecting a known quantity of SRC on the column followed by evaporating to dryness and weighing each fraction, the weight distribution of each fraction and the total percent recovery were determined. Approximately 50% of THF-soluble SRC is recovered in fraction No.3. In a typical experiment, 0.93 g was injected on the column and

0.92 g of material was reclaimed leading to a 99% recovery.

In an effort to circumvent the problem of partial THF decomposition, another solvent system was sought which would dissolve an appreciable fraction of SRC and at the same time be compatible with Bio Beads S-X4 and not be accompanied by solvent degradation. The SRC under investigation was found to have an appreciable solubility in CHCl_3 (72%). This soluble material was separated on a Bio Beads S-X4 column packed with a THF slurry of the beads followed by CHCl_3 wash. The chromatogram obtained when 0.92 g was injected was strikingly similar in retention time and features to the chromatogram where THF served as the solvent. Collection points for the four fractions were identical to those in the THF separation with 95% total recovery. The fractional weight percent of the total recovered for each fraction is shown in Table I. A comparison suggests that even though less SRC dissolves in CHCl_3 than THF, the distribution by weight within each soluble portion is surprisingly the same for THF and CHCl_3 soluble SRC.

One might be tempted to think that the molecular composition in fractions 1 and 1', 2 and 2', etc. are identical; however, this is apparently not the case as evidenced by subtle solubility differences coupled with NMR and ESR differences. The most telling data which support this conclusion are the number average molecular weights of these fractions taken in CHCl_3 . Considerably higher molecular weights are obtained from fractions collected on CHCl_3 -soluble SRC with CHCl_3 elution. A possible explanation

Table I. Molecular Weights and Percentage Distribution of Sized Fractions of THF-Soluble And CHCl_3 Soluble SRC on Bio Beads S-X4

<u>Fraction No.</u>	<u>Molecular weight^a</u>		<u>Total Amount recovered, %</u>	
	<u>THF</u>	<u>CHCl_3</u>	<u>THF</u>	<u>CHCl_3</u>
1	711	1550	19.8	19.3
2	487	1460	24.8	26.9
3	388	506	49.3	49.7
4	250 ^b	-	6.1 ^c	4.1

^aAverage of two independent measurements. Duplicate determinations differ by less than 5% in each case. ^bLower limit due to contamination with THF decomposition products. ^cCorrected for the presence of THF decomposition products.

of these results is that acid-base complexes have been postulated to exist in coal products which could account for this increase in molecular weight as measured in CHCl_3 . In an effort to expand and improve our separations we have conducted studies employing 36 inch preparative size tapered columns. Specific samples for this study were tetrahydrofuran and chloroform soluble SRC and acid-base-neutral fractions of Pittsburgh and Amax SRC. An enhanced separation was obtainable in going from a 6 to a 36 inch column using the same coal and packing materials. While greater resolution between large and small size molecules has been obtained, the resolution within each group has not been signifi-

cantly improved. The net effect seems to have been a "spreading-out" of the material eluted from approximately 70 ml on the 6 inch column to 180 ml on the 36 inch column. This is supported by the fact that a weight profile reveals significant material eluting from the column at all volumes. Proton FT NMR spectra of various 1 ml fractions throughout the elution range suggested at best minor improvements toward simplifying the fraction mixtures when compared with the six inch column. An important characteristic of these fractions is the progression from high aliphatic hydrogen to aromatic hydrogen content as the average molecular weight of the fraction decreases as monitored by ^1H FT NMR.

GPC separation via THF elution coupled with weight profile analysis on Amax CHCl_3 soluble SRC was next attempted. Since CHCl_3 dissolves only 80% of SRC compared to 93% for THF, a simpler starting coal sample was envisioned. In addition it was believed that the higher molecular weight-less soluble coal liquid would be excluded from the chromatography sample. The fraction of large size molecules, in fact, decreased relative to the smaller molecules; however, the range of "sized" molecules coming from the column for THF and CHCl_3 soluble Amax appears to not have changed based on a comparison of sample eluted volumes. In other words, CHCl_3 extraction does not totally exclude only large size molecules. Again ^1H FT NMR analysis of 1.0 ml fractions indicated very complexed fractions and an increase in aromatic content in going to the smaller molecular-sized materials.

While a more selective solvent extraction may result in a better overall separation, one naturally begins to examine a smaller and smaller percentage of the whole coal liquid which is not in keeping with our original premise.

I-C. Acid-Neutral-Base Fractionation of SRC

An acid-neutral-base separation of Pittsburgh and Amax THF soluble SRC has been developed. The method is in principle very much like Sternberg et al.; however, it differs considerably in practice. For example Sternberg's procedure involved only asphaltene toluene soluble coal liquids; whereas, our procedure deals with approximately 95% of the original coal liquid dissolved in THF. The initial step involves precipitation of the basic materials from THF with HCl(g) at atmospheric pressure. In order to avoid "salting-out" a minimum amount of neutral materials and to be as consistent as possible from one run to the next, 0.2 liter of HCl(g) per gram of dissolved SRC was reacted. After several hours the insoluble basic hydrochloride salts were filtered from the soluble acids and neutrals.

The basic HCl precipitate was suspended in basic ($\text{pH} > 13$) salt water (3 NaOH :10 NaCl :50 H_2O) and continuously extracted with THF to yield a black THF layer, a colorless H_2O layer and a dark-colored precipitate. A portion of this precipitate could be dissolved by re-suspension in H_2O ($\text{pH}=6$) followed by THF extraction. This behavior is suggestive of amphoteric materials. The original

hot THF layer was filtered then evaporated to dryness. The dry precipitate was stirred with warm water for 12 hours, in order to remove extraneous chloride ion, followed by filtration of the precipitate. This precipitate was washed with water until a negative test for chloride ion was obtained. The SRC bases were then re-constituted in THF, filtered, solvent removed and dried in vacuo at 75°C.

The THF filtrate containing SRC neutrals and acids was initially extracted with basic (pH>13) salt water to yield a black THF layer, a black H₂O layer and insoluble material which was removed by filtration. The THF layer which contained SRC neutrals was evaporated to dryness, washed to remove residual chloride ion and reconstituted in the same manner as the SRC bases. The insoluble material and H₂O layer were combined, acidified and extracted with THF. The black THF layer which resulted was evaporated, washed and reconstituted as described above to yield SRC acids.

Chlorine analysis suggests very little, if any, incorporation of chloride into each fraction in spite of exposure to HCl(g) and aqueous chloride solutions. Chlorine analysis on SRC prior to the separation scheme revealed the presence of comparable amounts of chlorine. Both Pittsburgh and Amax SRC give similar weight distributions of acids-neutrals-bases (5-50-20). Several points should be noted which support our acid-neutral-base designation. Acids and bases are considerably less soluble in THF and CHCl₃ than neutrals. Bases have 1-2% more nitrogen than acids or neutrals;

while, acids probably contain more oxygen as reflected by the much lower percent carbon relative to the bases and neutrals. Molecular weights via vapor phase osmometry in THF and CHCl_3 have been obtained on selected components at three different concentrations (Amax neutrals - 459, Amax bases - 499, Pittsburgh neutrals - 542). It is interesting to note, where solubility allows, that molecular weights in CHCl_3 were greater than in THF. Higher molecular weights in a solvent of lower donor strength suggests that these coal liquids, as some other recently studied asphaltenes, may associate via some intermolecular mechanism.

I-D. Size Exclusion Chromatography of SRC Fractions

Neutral and basic components were further separated via GPC (Bio Beads SX-2) on the 36 inch column mentioned above. Somewhat better chromatographic resolution is obtained on the neutrals and bases relative to SRC. This is especially apparent with the smaller "sized" molecules. Elution volumes are considerably larger for neutrals and bases than for THF and CHCl_3 soluble Amax SRC. This finding may be due to the fact that more intermolecular association is occurring in the latter products than in the neutrals or bases product. If this were the case one might conclude that separation of neutrals, acids and bases precludes an association possibility. Alternatively changes in column packing characteristics or coal liquid solution behavior between components may account for this. The similar number average molecular weights for each

sample indicates that the latter may be the case.

The amount of initially eluted material (e.g. larger size) appears to be about the same relative to the smaller sized material for neutrals and bases. In other words neutrals and bases consist of both large and small "sized" components. The enhanced resolution suggested for the smaller neutral molecules from their chromatogram is conclusively supported by the weight profile data in the same region. Again, it should be emphasized that just because neutrals and bases in solution have similar number average molecular weights, chromatograms and chromatographic weight profiles, this does not imply that neutrals and bases are of approximately the same size.

Selected 1.0 ml fractions from the neutrals and bases separation were analyzed via ^1H FT NMR analysis. For THF soluble Amax SRC 1 ml sample cuts from the 3 foot column indicate a low aromatic to total hydrogen ratio (~ 0.1) for the higher molecular weight fractions which increases to approximately 0.5 in the low molecular weight fractions.

Cursory examination of these spectra suggest that the 1 ml fractions still represent a complex mixture of compounds. However, a prominent feature apparent in most of these fractions is the broad, but nearly separate pattern between 3.5 to 4.5 ppm. A more informative comparison of this spectral region is evident for the 1 ml fractions obtained at approximately the same chromatographic elution volumes for the Amax neutrals and bases.

Integration of the spectral regions from 3.5 to 4.5 ppm indicate that 7% and 14% of the total hydrogen content for the Amax neutrals and bases, 1 ml fractions respectively, have ^1H chemical shifts in this region. The higher value for the Amax bases is typical for other chromatographic fractions for the bases and could indicate the greater preponderance of aromatic amine hydrogens assumed present in the bases. This is also consistent with the higher nitrogen content found for the bases by elemental analysis. It should be noted that the aromatic to total hydrogen ratios are roughly the same (0.31 and 0.33) for the same elution volumes. Unfortunately, the limited size of these samples (1-3 mg per 1 ml fraction) prevents quantitative ^{13}C FT NMR examination of these 1 ml fractions.

Oils, asphaltenes and preasphaltenes from Amax SRC were also subjected to size separation employing Bio Beads and differential refractive index detection. Again material is continuously eluted from the totally excluded to the totally permeated region for asphaltenes and preasphaltenes. Most of the oils, however, elute near the totally permeated region. With ΔRI detection we are unable to determine the relative concentration of large to small "sized" molecules. Nevertheless, it seems significant that Bio Beads is most capable of distinguishing between these classical fractions of coaly matter. The appearance of the chromatogram is markedly dependent on the eluting solvent. Even though exclusion limits in pyridine were double those in THF, asphaltenes

show excluded material in both solvents. The absence of the sharp spike in the pyridine chromatogram might suggest that there is less excluded material than for the comparable separation in THF.

II-A. Fluorine Tagging and ^{19}F NMR of SRC Models

During the past decade several NMR approaches have been suggested to characterize organic functionality (e.g., phenols, alcohols, carboxylic acids, etc.) present in organic compounds and/or mixtures. Nearly all of these approaches rely on the chemical shift parameter to distinguish molecular environment differences for an NMR probe nuclide either present in the functional moiety of interest or by tagging via an appropriate derivative.

Based on NMR sensitivity considerations alone, both the ^1H and ^{19}F nuclides are attractive candidates in studies of this type. However, ^{19}F NMR has potentially two advantages in comparison with ^1H NMR. First, the ^{19}F chemical shift parameter is generally more sensitive to subtle changes in molecular structure. A second advantage of ^{19}F NMR is the virtual absence of fluorine in most analytical samples of interest (e.g., coal, petroleum, and biological samples, etc.). This alleviates an inherent background problem when compared with ^1H and ^{13}C NMR approaches.

We have developed a new ^{19}F NMR reagent, trifluoroacetyl chloride, which yields the following derivatives

where X = O, S, or N. One of the major advantages of this reagent is the ease of derivative preparation. The derivatives are easily prepared in situ by bubbling the reagent gas (bp, -18°C) into a solution of the sample and solvent at low temperatures. For most alcohols, derivative preparation in high yields is easily accomplished in a variety of solvents including chloroform or chloroform-d, and tetrahydrofuran. However, we have observed that addition of tertiary amine bases (e.g., 2,6-lutidine) catalyze the reaction by either facile formation of the proposed intermediate trifluoroacylium ion and/or neutralization of the hydrochloric acid by-product. In the presence of 2,6-lutidine, alcohols, phenols, thiols and primary and secondary amines all readily react in reasonably good yields with trifluoroacetyl chloride under mild conditions.

The yields for the alcohols are nearly quantitative in every case except for the more hindered alcohols (e.g., tert-butyl alcohol). This is true regardless of whether 2,6-lutidine is present in the sample preparation. However, the rate of derivative formation is much faster in the presence of the 2,6-lutidine.

The ^{19}F chemical shift data for the trifluoroacetate derivatives of phenols cover a range of ~0.5 ppm. The derivatives containing an ortho substituent generally exhibit decreased shielding relative to the unsubstituted phenol (e.g., o-cresol

-7.40 ppm and phenol -7.55 ppm). An exception to this trend is 2-phenylphenol which resonates at higher field. In addition, a decrease in shielding is generally observed for larger fused aromatic ring phenols (e.g., α and β -naphthol). These results probably reflect the critical dependence of the geometric orientation of the trifluoroacetyl group relative to the aromatic ring-current. The para substituted phenols exhibit significant variations presumably reflecting the electron donating or withdrawing ability of the substituent. In addition, it should be noted that the high yields exhibited by the phenols are crucially dependent on the presence of the 2,6-lutidine. In the absence of 2,6-lutidine, the yields are usually less than 15%.

Although primary amines react in a normal manner in the presence of 2,6-lutidine providing monotrifluoroacetamide derivatives with ^{19}F chemical shifts ranging from -8.28 to -8.98 ppm, the secondary amine derivatives exhibit ^{19}F chemical shifts at significantly lower shielding ($\sim +0.4$ to -5.2 ppm). The importance of resonance form (b) below for the trifluoroacetamides of secondary amines is the most probable explanation for the large downfield ^{19}F chemical shifts observed for these derivatives.

(a)

(b)

2,6 LUTIDINE CATALYZED REACTION OF TRIFLUOROACETYL
CHLORIDE WITH ACTIVE HYDROGEN FUNCTIONAL GROUPS

Figure 2

In order to estimate the relative reactivity of the trifluoroacetyl chloride reagent with various functional groups, mixtures were prepared containing equimolar quantities of n-butyl alcohol, benzyl alcohol, phenol, n-butylamine, and diethylamine. Figure 2a is the ^{19}F spectrum obtained after 2.3 h in the absence of any 2,6-lutidine. This spectrum as well as the corresponding spectrum obtained after initial addition of the trifluoroacetyl chloride (~ 20 s) indicates nearly complete reaction of the alcohols (n-butyl alcohol and benzyl alcohol). The other components in the mixture do not react at a measurable rate, except for phenol which achieves a yield of $\sim 15\%$ after 2.3 h.

The ^{19}F spectrum presented in Figure 2b was obtained after 1.3 h in the presence of 1 molar equivalent of 2,6-lutidine. In this case, the reaction was virtually complete for all components in the mixture except for diethylamine. The ^{19}F spectrum in Figure 2c is for the case of 5 molar equivalents of 2,6-lutidine after 1.9 h added reaction time. All components of the mixture have reacted; however, the diethylamine derivative which did not react for the conditions of Figure 2a and 2b achieves an initial yield of 50% (~ 30 s) and a final yield of $\sim 80\%$ (Figure 2c).

The results of this study demonstrate the potential utility of ^{19}F NMR for characterizing various functional groups. That is, the ^{19}F chemical shift parameter for trifluoroacetyl derivatives is sufficiently sensitive to allow distinctions within a given

series (e.g., alcohols) dependent upon the number and type of moiety present at the carbon atom containing the heteroatom. This is apparent from the chemical shift ranges presented in Figure 3 which include all derivatives except for the secondary amines. The general trend of progressive shielding for phenyl, benzyl, and alkyl substitution, respectively, at the carbon bearing the heteroatom (i.e., oxygen, sulfur, or nitrogen) is clearly indicated in Figure 3. However, spectral overlap of certain functional groups containing different heteroatoms (e.g., secondary alcohols and alkyl thiols) is also readily apparent. Thus, for samples which are complex mixtures, the trifluoroacetyl chloride reagent would appear to be most useful when a preponderance of one type of heteroatom (e.g., oxygen) is present in the sample of interest. The generally high yields, the modest range of ^{19}F chemical shifts (~ 2 ppm for all derivatives except secondary amines), and ease of derivative preparation suggest an important role for trifluoroacetyl chloride for functional group analysis.

II-B. Fluorine Tagging and ^{19}F NMR of SRC Fractions

As previously indicated, the ^{19}F NMR chemical shift parameter is very sensitive to changes in the R and X groups for the trifluoroacetate or trifluoroacetamide derivatives. Based on our model compound approach, the trifluoroacetylation ^{19}F NMR method has been applied to a wide variety of solvent refined coal fractions. These include (1) process solvent and tray

¹⁹F CHEMICAL SHIFTS OF
TRIFLUOROACETYL DERIVATIVES

Figure 3

wash from the Amax SRC process, (2) Amax SRC, (3) THF soluble Amax SRC, (4) oils, asphaltenes, preasphaltenes, (5) "sized" fractions of Amax SRC, and (6) selected SESC fractions from a silica gel separation.

Application of the trifluoroacetylation technique to the process solvent, light organic solvent, and tray wash #3 (a distillate cut) reveals only phenolic functionality. As might have been expected, the process solvent exhibits the highest number of different phenols while the other two liquids have only specific components found in the process solvent.

The ^{19}F NMR spectrum for derivatives of Amax SRC illustrates a number of features observed in each normal spectrum. Three peaks appear which are not SRC derived. These fall at 0, -4.03 and -8.72 ppm and may be assigned to 1,2-difluorotetrachloroethane (chemical shift reference), α,α,α -trifluoroacetophenone (integration reference) and trifluoroacetic acid (trace of moisture), respectively. If the samples are not degassed subsequent to trifluoroacetylation, a fourth non-SRC-derived peak (-7.95 ppm) due to unreacted trifluoroacetyl chloride is observed.

The usefulness of the ^{19}F NMR technique as a mode of detection for various types of SRC fractions is illustrated below. Examination of "sized" fractions (e.g. #1-high MW, #2, #3-low MW) reveal little absorption chromatography accompanied the size exclusion phenomenon. Each fraction exhibited basically the same functionality with no particular fraction showing a preference for one functionality.

Application of this technique to SRC oils, asphaltenes and asphaltols leads to similar observations. It should also be noted that the trifluoroacetylation technique is amazingly sensitive to chromatographic solvent impurities. For example, THF decomposition products are observable in some of our samples which have been heated to 75°C in vacuo.

The SESC technique (Mobil Oil Co.) offers one method for separation of a coal liquid according to functionality. Selected fractions have been trifluoroacetylated and their ^{19}F NMR spectrum measured. The designation of SESC fractions #1 and #2 as aliphatics and aromatics, respectively, is consistent with our trifluoroacetylation techniques. No heteroatom functionality is apparent in #1 and only a relatively small quantity of phenols is found in #2. SESC fraction #5 exhibits nearly exclusively oxygen functionality. The broad unsymmetrical peak centered at -7.30 ppm falls in the range for phenols. The greater absorption to the low field side of this peak could suggest a fair amount of fused ring phenols (e.g. naphthols) in addition to mono-ring phenols. The absorption centered around -7.93 ppm is in the region for benzyl alcohols and primary alcohols. The major peak (-7.93 ppm) occurs exactly where the ethyl alcohol derivative appears and may, in fact, be due to residual ethyl alcohol since this fraction was eluted with $\text{Et}_2\text{O}/3\% \text{ ETOH}$. It is crucial to recognize that there is an abundance of phenols in this fraction even though the major compound type has been assigned to basic nitrogen heterocycles. In progressing to SESC fractions #8 and #9 total phenolic content appears to decrease, whereas, secondary amines are apparent in the latter fractions. Thus, although solvent

impurity derivatives (e.g. -7.93, trifluoroacetate of ethanol) partially obscure the aliphatic and benzylic alcohol regions (~ -7.7 to -8.4 ppm), it is clear that phenolic content maximizes in SESC fractions 3-5 as indicated in Figure 4.

II-C. Quantitative ^1H and ^{13}C NMR of SRC Fractions

The established utility of ^1H and ^{13}C NMR for characterization of coal products is well documented. Unfortunately, high-resolution ^{13}C FT NMR is not normally quantitative under operating conditions typically used. (It should be noted that quantitative ^1H FT NMR measurements also are not obtained routinely. The problem of variable spin lattice relaxation times (T_1 's) is present also in ^1H FT NMR. In addition, the greater signal intensity of ^1H NMR in comparison with ^{13}C FT NMR poses an additional potential problem of detector linearity in the ^1H FT NMR receiver). For ^{13}C FT NMR, variable spin lattice relaxation times (T_1 's) and nuclear Overhauser effects (a result of pseudo random ^1H noise decoupling) usually cause wide variations in signal intensity from line to line within a given spectrum. To overcome this problem, addition of a paramagnetic relaxation reagent to the NMR sample along with a gated ^1H decoupling sequence provides a method for obtaining quantitative ^{13}C NMR data. This technique in conjunction with the addition of a standard to the NMR sample provides a method for obtaining a number of important molecular parameters such as total, aromatic, and aliphatic hydrogen to

Figure 4

carbon ratios, $(H/C)_{\text{tot}}$, $(H/C)_{\text{ar}}$, and $(H/C)_{\text{al}}$, respectively. In addition, if weighed quantities of the SRC fraction as well as the reference standard are used, weight percent carbon and hydrogen values can be determined without recourse to elemental combustion data. This is an important consideration for studies of complex mixtures encountered usually in studies of coal products since the solution NMR measurements may not reflect the bulk results obtained by elemental combustion.

We have utilized weight percent carbon and hydrogen data obtained directly from NMR spectra to provide a means of "checking" whether all the carbon or hydrogen is observed in the NMR experiment relative to bulk elemental combustion analysis. This is an important consideration since the NMR measurements are normally solution measurements and coal liquids are known to precipitate on standing in certain solvents. The weight percent carbon values obtained from direct ^{13}C NMR measurements on different but chromatographically the same samples (i.e., sized fraction #3) of Pittsburgh, Western Kentucky, and Illinois SRC were in fair agreement with elemental combustion data. However, major deviations were observed for Amax and Monterey SRC Fraction #3 samples. The problem for the Amax sample is indicated in Figure 5, which is a plot of the ^{13}C integrated intensity ratio of the Amax sample and the reference (hexamethyldisiloxane) ($I[C_r/C_s]$) at two different temperatures vs. the weight ratio of the reference to sample (g_r/g_s). The solvent employed was chloroform-d.

^{13}C NMR STANDARD ADDITION
FOR AMAX 30 SAMPLE

Figure 5

Ideally, this plot should be linear with an intercept of zero where the slope provides the weight percent carbon from the equations below:

$$\text{slope} = \frac{\#C_r}{MW_r} \times \frac{MW_s}{\#C_s}$$

$$\text{wt \% C} = \frac{\#C_s}{MW_s} \times 1200$$

Below a (g_r/g_s) ratio of 0.35, the slope for both the high (75°C) and low (32°C) temperature results are in reasonably good agreement. At these low gram ratios, both slopes yield weight percent carbon values in good agreement ($\pm 5\%$) with elemental combustion data. The slope, however, changes dramatically above (g_r/g_s)^{-0.35} for the 32°C case and to a lesser extent for the 75°C case. After examination of the quantitative ^{13}C NMR procedure for possible sources of error in terms of the NMR instrumentation and applying the technique in several model compound studies, we concluded that this problem is probably due to an inhomogeneous solution (e.g., colloidal suspension) from the NMR point of view. Two sources of nonhomogeneity can be envisioned. These are (1) partial precipitation of the coal during the NMR measurement and (2) incomplete solubility of the reference in the solvent. For this particular Amax sample, the former possibility appears to be more likely and suggests that as much as 20 to 30% of the total carbon content is not observed in the 32°C experiments. It should

be noted that the solutions employed in the NMR experiment were always carefully filtered.

The incompatibility of the particular solvent and reference combination employed does not represent the total problem, since the aromatic to aliphatic carbon ratios (C_{ar}/C_{al}) and aromaticity (f_a) values deviate more severely at the lower temperature and higher $[(g_r/g_s)]$ ratios. These results suggest that molecular parameters obtained via a single NMR spectrum at an arbitrarily chosen sample concentration should be viewed with caution. It should also be noted that the Amax Fraction #3 examined in this study is a relatively low molecular weight fraction. It was not possible to obtain ^{13}C FT NMR data in chloroform-d for higher molecular weight fractions because of severe solubility limitations.

II-D. High Temperature ^{13}C NMR of SRC Fractions

Based in part on the results described above, ^{13}C FT NMR examination of these SRC samples at elevated temperatures as "melts" or dissolved in high temperature solvents was explored. With our present ^{13}C NMR probe ($\sim 300^\circ C$ limit) direct examination of the Amax Fraction #3 was feasible. No reference or solvent was employed in obtaining this spectrum. We have estimated a saving in time by at least a factor of 4-5 for the Amax SRC Fraction #3 melt ^{13}C spectrum in comparison with the normal solution chloroform-d ^{13}C spectrum for equivalent signal-to-noise ratios. Thus, in this particular example, the lower signal-to-noise ratio expected at elevated temperatures is more than equalized by the greater quantity

of sample within the active region of the ^{13}C receiver coil for the high temperature case. The higher signal-to-noise is also suggested by the relatively flat base line in the integral spectrum. A measured value of 0.80 for the aromaticity (f_a) for this spectrum is in reasonably good agreement with the solution values at 75°C.

Based on the melting range data, direct ^{13}C FT NMR examination of melts of the other fractions (#1 and #2) has not been attempted to date. An alternate approach was explored using phenanthrene as a solvent (~1:1 gram ratio of SRC sample and phenanthrene), since phenanthrene is known to be a good high temperature solvent for coal and coal products. Although the spectral lines for phenanthrene largely mask the aromatic region for Fraction #1 (180°C), the features in the aliphatic region are clearly discernible upon closer examination of this region. In particular, a relatively sharp peak at 29.7 ppm dominates the aliphatic region. (Value obtained relative to phenanthrene C_9 carbon $\delta_{\text{TMS}} = 127.2$ ppm) This particular peak also dominates the Amax #2 spectrum and to a lesser extent the fraction #3 spectrum. We have performed a ^1H off-resonance ^{13}C spectrum decoupling experiment which is consistent with the assignment of this signal as methylene carbons.

A ^{13}C NMR examination (Figure 6) of the total tetrahydrofuran soluble portion of the SRC product was accomplished by obtaining a melt of the SRC sample (1.2g) with 0.4g of $\text{DMSO-}^{12}\text{C}_2\text{-d}_6$ added at 140°C. Cycling of this sample between room temperature

Figure 6

and the elevated temperature over a 24-h period did not alter the measured aromaticity ($f_a=0.86$) by greater than 0.01 aromaticity unit. Since this sample represents a mixture of Fractions #1, #2 and #3, the measured aromaticity for this sample when compared with the value of 0.80 for Amax Fraction #3 indicate that the larger molecular weight fractions (#1 and #2) contain a higher degree of aromatic carbon content.

Previously we obtained ^1H FT NMR spectra for these fractions, which indicated a characteristic progression from high aliphatic hydrogen to relatively high aromatic hydrogen content as the average molecular weight of the fractions decreases. The previous ^1H FT NMR results have been interpreted in terms of two possibilities, either increasing aliphatic carbon content or progression to large polycondensed aromatic ring systems (i.e., low (H/C) aromatic ratios with relatively few aromatic hydrogens) for increasing average molecular weight for these fractions. The elevated ^{13}C FT NMR results now indicate that the latter possibility is more likely.

II-E. Liquid Chromatography of Coal Products with ^1H NMR Detection

The feasibility of utilizing a nuclear magnetic resonance spectrometer directly coupled to a liquid chromatograph has been determined. One major advantage of this approach is the enormous savings in time when compared to the tedious process of individual chromatographic fraction collection, solvent evaporation, and preparation for static NMR or other spectroscopic examination.

In addition, a second advantage was not appreciated until completion of the initial phases of this work. Namely, a given chromatographic peak as detected utilizing conventional detectors (e.g., Refractive Index) is further resolved using the NMR detector and provides a profile of components contained within this given chromatographic peak.

Obvious consideration in LC-NMR is solvent selection. Freon 113 (1,1,2 trifluoro-trichloroethane), d_1 -chloroform and carbon disulfide are possible solvent candidates which span a fairly wide range of polarity. Although perhaps too expensive to use neat (even with recycle), d_4 -methanol could serve as a polar modifier at a level of several percent. All separations involving deuterated solvents can be optimized with the cheaper protonated analogues prior to LC- ^1H NMR analysis. Chemical shift references such as tetramethylsilane (TMS) may be added directly to the mobile phase with negligible effect upon elution characteristics so long as the reference does not strongly interact with the stationary phase. Similarly, quantitative references may also be added.

Jet fuel samples supplied by the Air Force Aero Propulsion Laboratory (Wright-Patterson Air Force Base, Ohio) and the Naval Research Laboratory (Washington, DC) served as samples in this feasibility study. A Merk Silica Gel 60 Size B (310mm x 25mm I.D.) column was used after solvent equilibration.

The spectrum for the original jet fuel mixture yields considerably less information than the LC- ^1H NMR profile for the

paraho shale jet fuel (JP-5) (Figure 7) with respect to differentiating individual compounds present. The spectra for the alkanes (files 5-12) do not indicate the presence of branched hydrocarbons (no methine shoulder ~ 1.5 ppm). It is, therefore, reasonable to conclude that all of the aliphatic compounds in this sample are linear alkanes. Files 7 through 12 suggest a steady progression from n-decane to n-hexane. Elution volumes of standard samples run under identical conditions confirm this order.

The aromatic envelope in the paraho shale oil sample contains 26% of the material by volume (ANSI/ASTM D 1319-77). The various compounds in this envelope elute over a broad range so the concentrations are relatively low. The signal to noise ratio for spectra of the aromatic envelope is, therefore, considerably less than that for the aliphatic envelope. Several generalizations can be made regarding the compounds present in this portion of the profile. Simple alkylbenzenes with short alkyl groups predominate early in the peak with a progression through the xylenes towards mesitylene with possibly some tetra and pentamethylbenzene (files 34-37).

We have also utilized the flow LC- ^1H NMR approach for a few coal product samples. Figure 8 is the LC- ^1H NMR profile for the volatile liquid products obtained from a SRC sample. The alkane region (files 6-10) indicates a high branched alkane content present in the latter files (e.g., 8-10). Files 11-15 suggest the presence of alkanes in these fractions which were not observed

LC - ¹H FT NMR FLOW DETECTION
OF JET FUEL PARAHIO SHALE OIL
JP. 5

Figure 7

LC-¹H FT NMR FLOW DETECTION
OF VOLATILE LIQUID PRODUCT
FROM SOLVENT REFINED COAL

Figure 8

in the jet fuel previously discussed. In addition, the alkyl aromatics (files 24-30) indicate the absence of alkyl chains longer than one carbon (methyl groups). Thus, these fractions consist chiefly of xylenes. Also, the methyl naphthalene fraction is relatively minor in comparison with the xylenes. It should be noted that more polar compounds (e.g., phenols) are undoubtedly still not eluted from the chromatographic column under the present conditions (Freon-silica gel).

PUBLICATIONS

The following publications have been supported in part by this grant.

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