

Chemical Constituents In Different Solvent Refined
Coals As A Function Of The Feed Coal

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The chemical characterization of the organic constituents in solvent refined coal (SRC) is currently a subject of major concern (1) in terms of understanding present SRC processes and coal processing in general. The heterogeneous semi-solid SRC product obtained from present pilot plants represents a formidable analytical problem for identification and quantification of the organic materials present in SRC solids. Ideally, chromatographic separation of every individual organic compound present in SRC solids would allow relatively easy identification via modern analytical tools, such as, ^1H and ^{13}C Fourier transform nuclear magnetic resonance (^1H and ^{13}C FT nmr) and mass spectrometry. The feasibility of this approach, however, is questionable even assuming ideal chromatographic resolution could be achieved in light of the enormous time, quantity of material and probably weight losses accompanying each chromatographic separation. These limitations are especially acute for studies which monitor changes in organic composition as a function of a particular coal process variable (e.g., temperature, solvent, feed coal, etc.). An alternate chromatographic approach involves partial separation of the complex coal product mixture into numerous fractions based on either functionality, polarity or effective molecular size. Characterization of chromatographic fractions from this partial separation still has an obvious disadvantage in terms of analytically describing "average" molecular parameters. Although chemical characterization in terms of "average" molecular parameters is certainly a less than ideal approach, it does provide a reasonable method of monitoring processing variables provided that chromatographic fractions of a given size or type (nonpolar, polar, etc.) can be easily separated with nearly quantitative recovery. The established utility of ^1H and ^{13}C FT nmr allows a convenient method of deducing important average molecular parameters, such as, H/C aliphatic and aromatic ratios as well as assessing the relative importance of a number of other organic functional groups, (e.g., carbonyl, hydroxyl, phenol, etc.).

In the present comparison study of the organic constituents in SRC solids as a function of the SRC processing feed coal, we have employed gel permeation chromatography (2,3) for separation of the SRC solids into fractions based on effective molecular size rather than organic functionality or polarity. This approach has the advantage of providing "sized" preparative fractions (0.5-2.0 grams) with nearly quantitative recovery of the injected material from the chromatographic column.

Relatively large quantities of material were necessary for measuring metal content via flameless atomic absorption and for determining the nature and concentration of the organic constituents via ^1H and ^{13}C FT nmr techniques (4) in conjunction with elemental combustion and average molecular weight (vapor phase osmometry) data. The five SRC samples derived from different feed coals were obtained from a pilot plant operating at Wilsonville, Alabama. The SRC samples were obtained from eastern feed coals (Pittsburgh #8, and Western Kentucky #9 & #14), Illinois feed coals (Illinois #6 and Monterey), and a western coal (Amox). Preparative separation of the tetrahydrofuran (THF) soluble portion of each SRC sample provided four fractions using Bio-Beads S-X4 as the column packing. The elution volumes were held constant for each chromatographic fraction collected regardless of the SRC sample employed. The weight percent distribution for fractions 10 through 40 which correspond to decreasing effective molecular size along with the THF insoluble fraction (-10) are presented in Table 1. As indicated by the data in Table 1, all the SRC samples are greater than 88% soluble in THF. Although considerable weight changes occur as a function of the SRC feed coal sample between

Table I
 Analytical Data For Molecular "Sized" Fractions of Various Solvent Refined Coals*

FRACTION #	PITTSBURGH #8	AMAX	W. KENTUCKY #9 & #14	ILLINOIS #6	MONTEREY
10	19.2 ^a (711) [0.82]	23.6 ^a (959) [0.79]	28.4 ^a (795) [0.81]	39.2 ^a (611) [0.83]	33.9 ^a (652) [0.85]
20	24.1 (487) [0.92]	16.4 (597) [0.85]	17.1 (408) [0.91]	20.0 (447) [0.88]	22.8 (556) [0.80]
30	47.9 (388) [0.93]	48.6 (547) [0.76]	38.3 (313) [0.90]	30.4 (385) [0.85]	40.7 (479) 0.89]
40	5.9	3.2	4.7	1.6	2.6
-10**	2.9 [0.70]	8.2 [0.62]	11.6 [0.72]	8.8 [0.73]	0

* Average molecular weight data in parenthesis via vapor phase osmometry. Hydrogen to carbon (H/C) total ratio data in brackets.

** THF insoluble fraction, percent solubility determined by suspending 1 gram of the SRC sample in 200 ml of THF and stirring for 3 hours. The resulting solution was filtered through a millipore filter (LWSP) and the residue was dried before weighing.

^aFractional weight percentage

fractions 10 and 30, the molecular weight data are relatively consistent for a given fraction. Some variations do, however, occur for the Amax and Monterey SRC samples.

In characterizing the organic constituents for the major soluble fractions, a cursory difference between the eastern coals (e.g., Pittsburgh #8 and W. Kentucky #9 & #14) with the western coal (Amax) is evident. The total hydrogen to carbon ratio (H/C) data obtained from elemental combustion are tabulated in Table 1 with the Amax SRC fractions consistently exhibiting the lowest (H/C) ratios for each fraction. The relatively constant nature of the SRC samples derived from the eastern and Illinois #6 feed coals is indicated by the relatively narrow range of average molecular formulas presented in Table 2. The Amax and Monterey SRC fractions are exceptions in this regard (Table 3) and have consistently larger molecular formulas for a given fraction as previously suggested by the molecular weight data in Table 1.

Table 2

Range of Average Molecular Formulas for Western Kentucky #9 & 14
Pittsburgh #8 and Illinois #6 SRC Fractions *

<u>FRACTION</u>	<u>FORMULA</u>
10	$C_{41-55}H_{35-45}O_{3.7-4.7}S_{0.2-0.4}N_{0.7-1.0}$
20	$C_{27-33}H_{24-30}O_{2.5-3.4}S_{0.2-0.4}N_{0.5-0.6}$
30	$C_{22-27}H_{20-24}O_{1.4-2.2}S_{0.1-0.2}N_{0.4}$

*Values based on average molecular weights and elemental combustion data

Table 3

Average Molecular Formulas For Amax and Monterey SRC Fractions

<u>FUNCTION</u>	<u>MONTEREY</u>	<u>AMAX</u>
10	$C_{43.4}H_{37.0}O_{4.5}$ $S_{0.3}N_{0.8}$	$C_{67.5}H_{52.7}O_{4.3}$ $S_{0.4}N_{1.0}$
20	$C_{38.0}H_{30.3}O_{2.6}$ $S_{0.6}N_{0.7}$	$C_{40.0}H_{34.0}O_{4.1}$ $S_{0.3}N_{0.6}$
30	$C_{34.2}H_{30.9}O_{1.5}$ $S_{0.2}N_{0.5}$	$C_{37.8}H_{34.0}O_{3.0}$ $S_{0.1}N_{0.5}$

*Values based on average molecular weight and elemental combustion data

The ^1H and ^{13}C nmr spectra superficially appear very similar for a given SRC fraction regardless of the feed coal. Typical ^{13}C and ^1H FT nmr spectra for Amax Fraction 30 are presented in Figures 1 and 2, respectively. Quantitative nmr measurements, however, indicate major changes do occur in the aliphatic and aromatic (H/C) ratios as summarized for fraction 30 samples in Table 4. The unusually low aliphatic (H/C) ratio for the Amax sample is very suggestive of highly condensed cyclic aliphatic networks (e.g., substituted adamantanes) previously suggested by a Mobile group (5).

Further trends and comparisons of the organic constituents will be the major thrust of this presentation with particular attention focusing on the Amax sample.

Table 4

(H/C) Aromatic and Aliphatic Ratios
For SRC Fraction 30 Samples*

SRC	(H/C) _{ALP.}	(H/C) _{ARO}	F _A (Aromaticity)
Pittsburgh #8	1.66	0.49	0.64
West. Kentucky #9 & #14	2.09	0.44	0.71
Illinois #6	1.35	0.57	0.64
Monterey	2.12	0.46	0.73
Amax	1.15	0.50	0.63

* Values obtained from quantitative ^1H and ^{13}C FT nmr measurements.

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FIGURE 1
 ^1H Spectrum of Amax Fraction 30

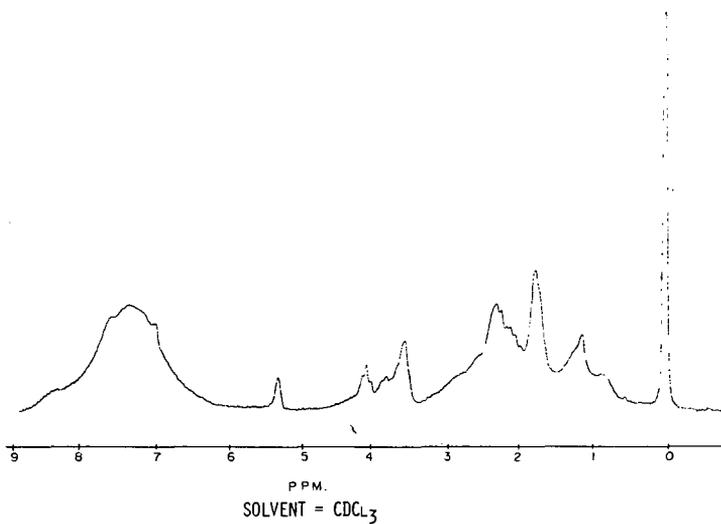


FIGURE 2
 ^{13}C Spectrum of Amax Fraction 30

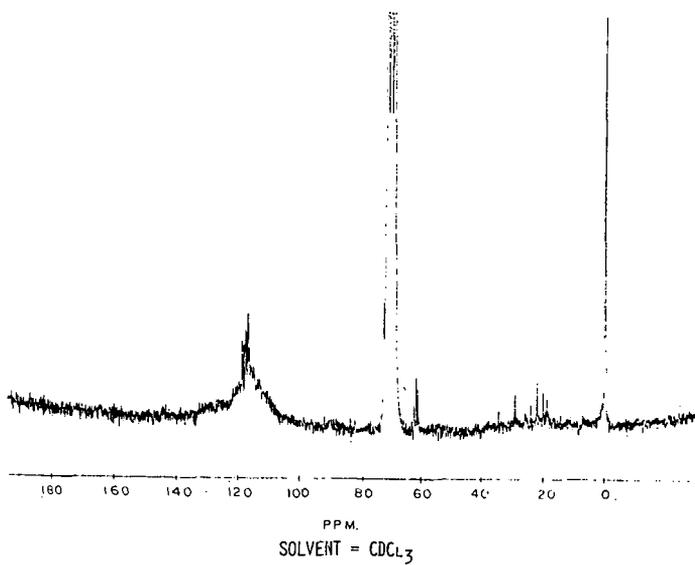


FIGURE 1
¹H Spectrum of Amax Fraction 30

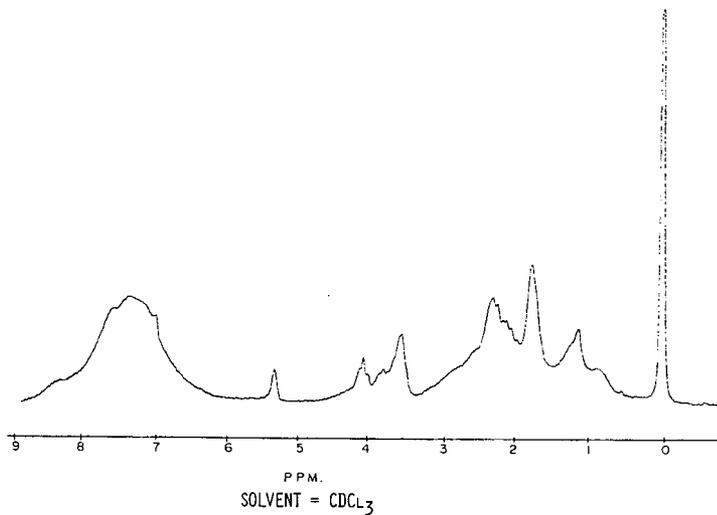


FIGURE 2
¹³C Spectrum of Amax Fraction 30

