A DETAILED STRUCTURAL CHARACTERIZATION OF HEAVY CRUDE ATMOSPHERIC TOWER BOTTOMS

by

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As the petroleum industry finds itself faced with increasing proportions of heavy sour crude, researchers must address the problem of how to upgrade this material to be compatible with existing refinery processes and product slates. The first problem to be faced in upgrading a heavy crude or residue is how to characterize the material well enough to understand the chemistry of the upgrading process. Crude residues are far more complex than coal liquids for they not only contain a variety of aromatic and heterocyclic units, but they also contain naphthenic and alkyl substituents of almost infinite variety on these simpler units as well as heavy alkanes.

The samples that will be discussed here were derived from a Maya (Mexico) crude (API gravity 19.1°). Since we are primarily interested in the chemistry of the residue, the crude was distilled at 680°F (360°C) to obtain an atmospheric tower bottom (ATB). The Maya ATB is 61% of the crude and has an API gravity of 7.7° and a sulfur content of 4.7%.

In order to simplify the characterization and upgrading chemistry, the Maya ATB was separated chromatographically into asphaltene, three acid, three base, neutral oil and neutral resin fractions on a preparative scale (1 kg) (1, 2). The separation yields and elemental analysis of the fractions are shown in Table I. A wide variety of characterization techniques were then applied to many of these fractions, including ^{1}H NMR, ^{13}C NMR (conventional and INEPT (3)), high resolution mass spectrometry (4) (HRMS), GC-MS (5), and atom specific GC (6).

Flame ionization detector (FID) and flame photometric detector (FPD) gas chromatograms of the Maya ATB neutral oil are shown in Figure 1 (5). The chromatograms were obtained on a Varian 3700 using a 10 ft long, 1/8 inch OD column packed with 10% OV-1 on acid-washed Chromasorb W. The FID trace shows an alkane series from n-C_{17} to n-C_{34} superimposed on a broad unresolved hump. The sulfur specific FPD trace shows some resolution of a few peaks at the low boiling end of the chromatogram and a similar unresolved hump. Other than the normal alkane series, no specific compounds were identified in the chromatogram. In spite of the rather small amount of information obtained on this sample, gas chromatographic techniques were found to be useful in monitoring changes in the hydrocarbon and sulfur species upon upgrading.

In order to eliminate interferences from saturates, the neutral oil was further separated into saturates, aromatics and polars by HPLC. This was done on a Waters HPLC using a dry silica (22-47 mesh) column.

The aromatic fraction was analyzed using a Kratos MS 50 high resolution mass spectrometer (HRMS) operated with an ionizing voltage of 70 eV, to obtain quantitative information on the aromatic and heterocyclic compounds in the neutral oil (4). Table II is a summary of the HRMS results, giving the weight percentage of the various species by Z number and the average number of carbon atoms in each Z class. For example, dibenzothiophenes were 3.32% of the sample and had an average of about six carbon atoms attached to the basic dibenzothiophene unit. Searching through the list of specific compounds in the sample reveals that dibenzothiophene accounts for 0.19% of the sample, methyl dibenzothiophene 0.43%, etc., through the series of alkyl dibenzothiophenes up to mass 408, C_{10} dibenzothiophenes. Several hundred individual mass peaks are identified by carbon number, Z class, heteroatom content and weight percentage. This specific information allows the monitoring of the reactivity of particular molecules or molecular types.

GC-MS was also applied to the aromatic cut of the Maya ATB neutral oil. A Finnigan 4500 system with a 60-meter DB-5 fused silica capillary column was used. Due to the poor GC separation (see Figure 1), few GC peaks could be identified. However, knowing the masses of the sulfur species in the sample from HRMS, specific ion chromatograms were generated to obtain isomer number information and to observe the relative reactivity of these isomers in hydroprocessing (6). Figure 2 shows the mass chromatograms for dibenzothiophene (DBT) (m/z = 184) and substituted DBT through C_7.

Proton and ^{13}C NMR spectra were obtained on most of the fractions from the Maya ATB on a Varian XL-200 FT NMR instrument. Table III gives some of the results from the ^{13}C NMR data on the fractions. Note that the neutral oils are the least aromatic fraction, being comprised of aromatics and "polars," which are only about one third aromatic, and 25% saturates, which gave no detectable signal in the aromatic region. Figures 3 and 4 show the normal ^{13}C NMR and INEPT spectra of the aromatic cut of the neutral oil (3). The INEPT technique causes the NMR signals due to CH and CH_3 to be inverted and virtually eliminates the signals due to carbons with no protons attached, such as those with a chemical shift around 140 ppm in the normal ^{13}C NMR spectra. A complete analysis of the spectrum gives much more structural detail.

The ^{1}H NMR spectrum of the Maya ATB neutral oil aromatics is shown in Figure 5. Although the spectrum is not rich in detail, due to the complex mixture in the sample, it can be analyzed by the technique of Clutter, Petrakis et al. to give average molecule information (7). These data are presented in Table IV. Compared to the ^{13}C NMR technique, the proton data give a somewhat lower aromaticity (0.27 versus 0.34) and a much lower (15.6% versus 28%) naphthenic carbon content. ^{13}C NMR techniques are believed to give the more reliable data. ^{1}H NMR, however, is better for determining the number of alkyl substituents.

While some of these types of data can be formally integrated to produce concentrations of functional groups (8), the general picture of the Maya ATB neutral oils that can be synthesized from the data is that the material is a very complex mixture of hydrocarbons and sulfur heterocycles. It contains about 25% saturates with alkanes from C_{17} to about C_{40}, alkyl

naphthenes, and very few isoprenoids. About 75% of the neutral oil is alkyl aromatics and thiophene-based compounds that are mostly from 1 to 5 rings, have some naphthene substituents, and are substituted, on the average in three to four positions with alkyl groups that range from methyl to about C_{16}. The ratio of methyl to longer chains is 1.5:1 and the average length of the alkyl chain is about 5. Qian et al. give data from an aromatic cut of a petroleum pitch which has similar aromaticity, but a higher molecular weight and longer alkyl chains (9).

Due to their very complex nature, these petroleum residues require extensive separation and as many analyses as are available and affordable. While their absolute accuracy in describing the molecules in the mixture may be subject to a variety of errors, the strength of the analytical techniques described here is in measuring changes in the molecular structures upon hydroprocessing.

References

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TABLE I

Yield and Elemental Composition of Maya ATB Fractions

Yield %	C %	H %	O %	N %	S %	Total	
Maya ATB	-	84.26	10.40	0.47	0.51	4.70	100.34
Neutral Oil	69.68	84.30	11.31	0.82	1.53	3.79	101.75
Asphaltene	24.14	82.65	7.83	1.41	1.12	6.97	99.98
Very Weak Base	0.86	81.78	9.42	2.48	0.15	5.00	98.83
Weak Base	0.07	49.49	6.32	18.95	0.30	6.04	81.10
Strong Base	0.01	53.98	6.86	12.87	3.34	7.55	84.60
Very Weak Acid	0.17	80.32	8.02	4.93	1.60	4.02	98.89
Weak Acid	0.04	61.81	6.65	14.13	0.85	1.72	85.16
Strong Acid	1.23	58.39	6.97	16.79	3.74	0.20	86.09
Neutral Resin	2.39	76.28	8.43	3.14	0.81	5.08	93.74
Total Recovery %	98.58						

TABLE II

High Resolution Mass Spectrometry Data on Maya ATB Neutral Oil Aromatics

Z #	Hydrocarbon Type	AV C #	Wt%	Total Wt
Monoaromatics				28.01
-6	Alkylbenzenes	14.03	12.75	
-8	Indans	15.37	7.08	
-10	Indenes	15.16	8.18	
Diaromatics				19.88
-12	Naphthalenes	15.96	7.79	
-14	Biphenyls	18.08	5.29	
-16	Fluorenes	18.80	6.81	
Triaromatics				10.61
-18	Phenanthrenes	19.86	4.48	
-20	Phenanthrocycloparaffins	20.78	6.13	
Tetraaromatics				7.48
-22	Pyrenes	21.50	3.54	
-24	Chrysenes	22.92	3.94	
Pentaaromatics				10.04
-26	Chrysocycloparaffins	24.48	3.77	
-28	Benzpyrenes	25.20	2.75	
-30	Dibenzanthracenes	26.48	3.52	
Polyaromatics				8.03
-32		25.73	3.53	
-34		27.07	2.29	
-36		28.40	2.21	
Thiophenes				15.35
-10S	Benzothiophenes	20.38	2.52	
-12S		20.41	2.59	
-14S		20.22	0.58	
-16S	Dibenzothiophenes	18.14	3.32	
-18S		20.47	1.28	
-20S		18.28	1.03	
-22S	Benzonaphthothiophenes	21.05	1.36	
-24S		22.65	1.15	
-26S		22.00	0.90	
-28S		23.97	0.62	
Phenols/Furans				0.60
-60	Phenols	6.00	0.04	
-160	Dibenzofurans	15.28	0.18	
-180		16.36	0.13	
-220	Benzonaphthofurans	18.56	0.25	

AV C NO 19.33 AV Z NO -16.88 C/H = 1/1.127

TABLE III

Carbon Distribution in Fractions by ^{13}C NMR

	% Aromatic		% Naphthenic	% Saturate
Neutral Oils			25% (calc)	
Aromatics	60.0*		34%	28%	38%
Saturates	25.7*		0%	34%	66
Polars	14.3*		32%	ND	ND
Very Weak Acid			62%	12	26
Weak Acid			54%	17%	29%
Strong Acid					
Very Weak Base			45%	22	33
Weak Base			44%	23%	33%
Strong Base			52%	ND	ND

*Percentage of neutral oil.

TABLE IV

Average Molecule Data on Maya ATB Neutral Oil Aromatics from ^{1}H NMR

Aromaticity:	0.27	% Monoaromatics:	43.8
Aromatic Rings/Molecule:	1.7	% Diaromatics:	46.9
Aromatic Ring Carbons/Molecule:	8.6	% Triaromatics:	9.3
Average Molecular Formula:	C31.7 H43.4	Average Molecular Weight:	423.9
% Alkyl Carbon:	72.8	Nonbridge Aromatic Carbons/Molecule:	7.3
Alkyl Substituents/Molecule:	3.6	% Subst. of Nonbridge Arom. Carbons:	57.8
Carbons/Alkyl Substituent:	6.4	Naphthene Rings/Molecule:	1.4
% Nonbridge Aromatic Ring Carbons:	23.1	% Naphthenic Carbon	15.6

NOTE: *Average mol wt is based only on C and H and does not account for O, S, N, etc.*

FIGURE 1

FID and FPD Chromatograms
of Maya ATB Neutral Oil

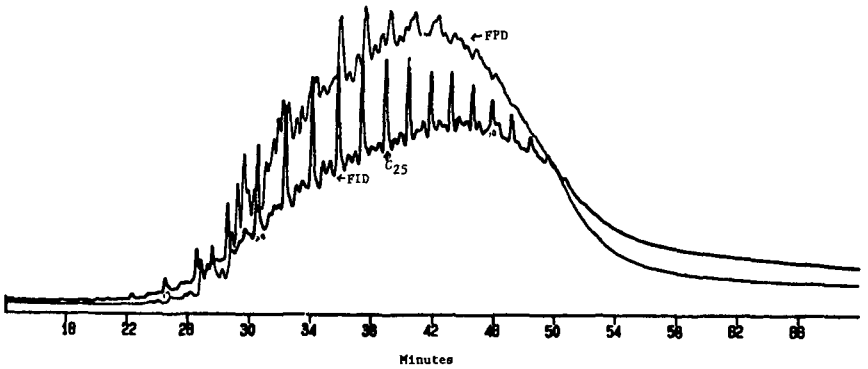
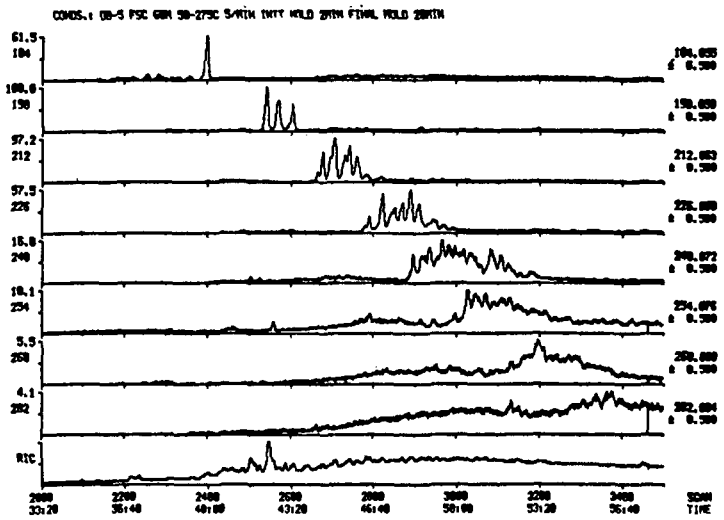


FIGURE 2

Specific Ion Chromatograms for Dibenzothiophene and
Substituted Dibenzothiophenes in Maya ATB Neutral Oil, Aromatic Fraction



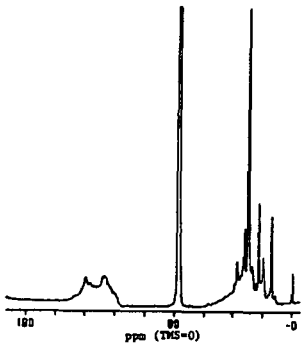


FIGURE 3

^{13}C NMR Spectrum of Maya ATB
Neutral Oil, Aromatic Fraction (50.3 MHz)

FIGURE 4

^{13}C INEPT Spectrum of Maya ATB
Neutral Oil, Aromatic Fraction (50.3 MHz)

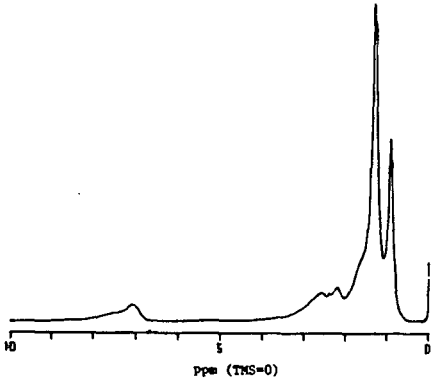


FIGURE 5

200 MHz ^{1}H NMR Spectrum of Maya ATB
Neutral Oil, Aromatic Fraction