

A COMPARISON OF NATURALLY OCCURRING  
SHALE BITUMEN ASPHALTENE AND RETORTED SHALE OIL ASPHALTENE

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INTRODUCTION

Asphaltene is usually defined as the pentane soluble and benzene insoluble fraction of crude oil. The molecular structure of this material has not yet been fully understood. Since asphaltene is generally recognized as the transitional stage from fossil fuel source to oil products (1,2), knowledge of the molecular structure of asphaltene is essential to the understanding of its occurrence and transition.

The majority of the organic material in oil shale is known as kerogen (organic solvent insoluble fraction). Bitumen (organic solvent soluble fraction) generally comprises only a small part of the total organic matter in oil shale. During retorting (thermal cracking), kerogen and bitumen undergo thermal decomposition to oil, gas and carbon residue. According to a number of investigators (3-5), the mechanism for thermal cracking of the oil shale is by decomposition of the kerogen to bitumen, gas and carbon residue and subsequently decomposition of the bitumen to oil, gas and coke. Asphaltene is ubiquitously present in both the natural occurring bitumen and the retorted shale oil. Very few cases for the comparison of asphaltene properties are available in the literature (6-8). In this research, a comparison of the shale bitumen asphaltene and the retorted shale oil asphaltene has been undertaken to investigate structural changes during thermal cracking.

It is anticipated that information obtained from this type of research will be helpful for the production and refining of shale oil. The role of asphaltene and its structure may be an useful indicator toward the severity of temperature effect during retorting or treatment.

EXPERIMENTS

A Green River oil shale from Anvil Points, Colorado was crushed to 8-20 mesh size prior to solvent extraction or retorting.

A. Solvent Extraction

The shale (130 g) was Soxhlet extracted with 90% benzene: 10% methanol (300 ml) for 72 hrs. Six sets of Soxhlet extraction were carried out to afford a total yield of shale bitumen 14.5 g.

B. Shale Retorting

The retort chamber is a cylindrical quartz column which is 47 mm in diameter and 300 mm in length with a screen of 20 mesh size welded in the bottom. Heat is transferred to the shale through the quartz wall wrapped with two heating wires connected to a transformer. A stainless steel sheathed chromel-alumel (type K) thermocouple is inserted through the side arm and is assembled such that the

tip is roughly in the middle of the retort. The temperature was raised rapidly to 425°C in one experiment and to 500°C in another experiment over half an hour and maintained these for three hours. Air enters through the top of the chamber at a flow rate of 1 ml/sec and moves downward together with the product oil through the cooling column. The product oil was collected at the bottom of the retort into a receiver. The product gas was passed through acid and base traps but was not collected. The collected oil was separated from the water phase by extraction with benzene in a separatory funnel.

#### C. Isolation of Asphaltene

The asphaltenes were isolated according to the modified procedure (9,10). A sample of the shale bitumen or retorted shale oil was precipitated with 20-fold volume of n-pentane. The oil/resin (pentane soluble) fraction was separated from the precipitate by filtration and soxhlet extraction with n-pentane. The asphaltene (pentane insoluble, benzene soluble) fraction was obtained by soxhlet extraction of the residue with benzene. In the following text, these asphaltenes will be abbreviated as Bitu, R<sub>425</sub>, and R<sub>500</sub> representing bitumen asphaltene and asphaltenes derived from shale oil retorted at 425°C and 500°C respectively.

#### D. Physical and Chemical Analysis

The elemental analyses were done by Elek Microanalytical Laboratories, Torrance, California. A Mechrolab Model 301A Vapor Pressure Osmometer was used to determine molecular weight. IR spectra were recorded at a concentration of 25 mg/ml in CH<sub>2</sub>Cl<sub>2</sub> using 0.5 mm NaCl cells on a Beckman Acculab 6 instrument. <sup>1</sup>H NMR spectra were obtained from a Varian XL-100 spectrometer with CD<sub>2</sub>Cl<sub>2</sub> as solvent and internal reference (residue peak at 5.3 ppm). <sup>13</sup>C NMR spectra were obtained from a Varian XL-100 unit, with built-in minicomputer, operated at 25.2MHz. For all samples CDCl<sub>3</sub> is used as solvent and internal reference (central peak at 77.2 ppm). A sample of asphaltene (0.5 g) was dissolved in 2.5 ml of CDCl<sub>3</sub> with 35 mg of Cr(acac)<sub>3</sub> added to it. To obtain reliable quantitative results, a delay time of 4 sec after each 35° pulse and 0.68 sec acquisition time was used in the gated decoupling sequence.

## RESULTS

Fractionation of the three samples afforded the asphaltene fraction constituting 7.3%, 0.39%, and 0.74% by weight for the shale bitumen, shale oils retorted at 425°C and 500°C respectively.

#### A. Elemental Composition

Elemental Analysis data for the three asphaltene samples - Bitu, R<sub>425</sub>, and R<sub>500</sub> are presented in Table I.

#### B. Infrared Spectra

Infrared spectra of the three asphaltene samples are presented in Figure 1 for comparison. A number of well defined bands appear in all three spectra. These bands are centered at 3600 cm<sup>-1</sup> attributed to phenolic O-H absorption, 3460 cm<sup>-1</sup> attributed to pyrrolic N-H absorption, 3180 cm<sup>-1</sup> attributed to hydrogen-bonded O-H or N-H absorption, 2925 cm<sup>-1</sup> and 2860 cm<sup>-1</sup> due to asymmetric and symmetric C-H stretching, 1800 cm<sup>-1</sup> to 1600 cm<sup>-1</sup> attributed to carbonyl C=O stretching, 1400 cm<sup>-1</sup> to 1480 cm<sup>-1</sup> attributed to C-H bending and 1375 cm<sup>-1</sup> attributed to symmetric bending of the methyl groups. Differences in the absorption intensities of these peaks among the three asphaltene samples are shown in Table II.

#### C. <sup>1</sup>H NMR Spectra

The proton nmr spectra of Bitu, R<sub>425</sub> and R<sub>500</sub> are shown in Figures 2-4. If contributions from protons associated with hetero-atoms can be discounted, proton

types in the nmr spectra can be divided into four groups: aromatic protons ( $H_A$ ), alpha alkyl protons ( $H_\alpha$ ), methyl protons in the gamma position or farther from the aromatic ring ( $H_\gamma$ ) and other alkyl protons representing primarily the methylene protons which are beta or farther from the aromatic ring ( $H_\beta$ ) (11). Fractional proton distribution were calculated directly from the integration curves. The separation point was chosen semi-empirically for the  $H_\alpha$  and  $H_\beta$  bands at 1.9 ppm and for the  $H_\beta$  and  $H_\gamma$  bands at 1.0 ppm from the determination of the band shapes and areas. Fractional proton distribution of the three asphaltene samples are presented in Table III.

#### D. $^{13}C$ NMR Spectroscopy

Carbon-13 nmr spectra of the Bitu and R500 samples are presented in Figures 5,6. For the carbon group assignments, we have used the scheme developed by Ladner and coworkers (12). Carbon distributions derived from the  $^{13}C$  nmr spectra are presented in Table V. Aromaticities determined directly by  $^{13}C$  NMR are 0.24, 0.51, and 0.60 for Bitu, R425, and R500 respectively.

### DISCUSSION

The results of the elemental analysis indicate that asphaltenes derived from retorted shale oils have smaller H/C ratio and smaller oxygen and sulfur contents, but greater nitrogen content than that derived from shale bitumen. It seems that some of the oxygen and sulfur are eliminated as water and hydrogen sulfide during the retorting process. It remains unclear (13) whether the greater nitrogen content arises from incorporation of nitrogen gas from the air or from temperature effect as suggested by Hill (14) - "Nitrogen in the kerogen is present in molecules of very high molecular weight which tend to remain in the shale at temperatures below 800°F."

The retorted shale oil asphaltenes have greater pyrrolic N-H and hydrogen bonded O-H or N-H absorption than the shale bitumen asphaltene as revealed in the IR spectra. Band shapes for the carbonyl stretching region of the three samples also show remarkable differences. Since it is well known that either hydrogen bonding or conjugation with an olefinic or phenyl group causes a shift of the carbonyl absorption at lower frequencies, the result seems to indicate a relatively greater proportion of hydrogen bonded and/or conjugated carbonyl groups for R425 and R500 than for Bitu. The  $CH_3/CH_2$  ratio is also increased for R425 and R500 than for Bitu as measured by absorbance at  $1375\text{ cm}^{-1}$ .

In combination with average molecular weight and elemental compositions, the  $^1H$  nmr data can be used to derive some average structural parameters: aromaticity ( $f_a$ ), degree of substitution of the aromatic sheet ( $\sigma$ ), number of carbon atoms per alkyl substituent ( $n$ ), ratio of peripheral carbon atoms per aromatic sheet to total aromatic carbons ( $H_{aru}/C_{aru}$ ), and number of aromatic ring per molecule ( $R_A$ ) can be calculated by the modified Brown-Ladner (15) method as described in Eq. (1)-(5).

$$f_a = \frac{C/H - H_\alpha/2 - H_\beta/2 - H_\gamma/3}{C/H} \quad (1) \quad \sigma = \frac{H_\alpha/2}{H_A + H_\alpha/2} \quad (2)$$

$$n = \frac{H_\alpha/2 + H_\beta/2 + H_\gamma/3}{H_\alpha/2} \quad (3) \quad \frac{H_{aru}}{C_{ar}} = \frac{H_A + H_\alpha/2}{C/H - H_\alpha/2 - H_\beta/2 - H_\gamma/3} \quad (4)$$

$$R_A = C_A \frac{1 - \frac{H_{aru}}{C_{ar}}}{2} + 1 \quad (5) \quad C_A = \text{total number of aromatic carbons}$$

In these calculations, it is assumed that each carbon atom alpha to an aromatic ring carries two protons. The atomic ratio of proton to carbon in the  $H_{\beta}$  fraction is also assumed to be 2. The calculated average properties are shown in Table IV. On the basis of these calculated average properties, the retorted shale oil asphaltenes have relatively higher aromaticity, lower degree of substitution of the aromatic sheet and shorter alkyl substituents. Based on these structural properties, the main reactions occurred in the retorting process are carbon-carbon bond fission and intramolecular aromatization.

The  $^{13}C$  chemical shift range 168-210 ppm contains carbonyl resonance which was observed in Bitu but not in R500, suggesting that carbonyl groups are very likely labile thermally. In the retorting process, the carbonyl groups may be involved in ring closure by intramolecular Friedel-Crafts acylation and subsequently reduced by hydrogen generated by aromatization within the system. The absence of the carbonyl resonance in the  $^{13}C$  nmr spectrum of R500 does not prove the absence of the carbonyl group in this sample, since carbonyl carbons generally have very long relaxation times and are undetectable by  $^{13}C$  nmr.

The chemical shift ranging from 148-168 ppm contains mainly resonances from aromatic carbons joined to hydroxylic or etheric oxygen. Both Bitu and R500 have the bulk of resonance occurred between 148 and 159 ppm indicating that there are much more phenols than aromatic ethers since the latter should resonate predominantly between 159 and 168 ppm. The percentage of phenolic carbon is greater for R500 (~2.8% of total carbons) than for Bitu (~1.1% of total carbons), which may account for the greater hydrogen bonding tendency of R500 as detected by IR.

In the aliphatic carbon region, the most prominent signal for Bitu is a sharp peak at 29.6 - 29.8 ppm attributed to methylene carbons  $\gamma$  or further from an aromatic ring and  $\delta$  or further from the terminal  $CH_3$  group in n-alkyl chains of at least 7 carbon long. The area under this peak is 6% of the total aliphatic carbons. The total intensity of the 9-22.5 ppm range attributed to methyl carbons accounts for 40.6% and 16.7% of the total aliphatic carbons for R500 and Bitu respectively. The result is consistent with a longer average alkyl chain length for Bitu as calculated by proton nmr.

A comparison of the aromaticity determined by  $^{13}C$  and  $^1H$  nmr reveals that although the agreement is rather good for R500, the aromaticity determined by  $^1H$  nmr is smaller than that determined by  $^{13}C$  nmr for Bitu. It is likely that since the aromatic proton ( $H_A$ ) of Bitu constitutes only a very small percentage of the total proton, the effect of phenol OH and amide NH to the content of  $H_A$  is accentuated. For Bitu, the aromaticity determined by  $^1H$  nmr is too large because contribution from phenol OH and amide NH to the  $H_A$  content is neglected in the above calculation. For R425 and R500, the effect of phenol OH and amide NH is perhaps compensated by the greater number of methyl substituents and therefore a good agreement in aromaticity is obtained. For Bitu, some of the average parameters would be in error as a result of the relatively greater contribution of phenol OH and amide NH to the value of  $H_A$ . For instance,  $f_a$  would be too high,  $H_{ar}/C_{ar}$  too low and  $R_A$  too large.

#### ACKNOWLEDGEMENT

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Table I. Elemental Compositions of Shale Oil Asphaltenes

	Bitu	R <sub>425</sub>	R <sub>500</sub>
C <sup>a</sup>	74.53	76.50	78.22
H <sup>a</sup>	8.86	7.97	7.02
N <sup>a</sup>	2.71	4.49	5.03
S <sup>a</sup>	1.80	1.37	1.08
O <sup>a,c</sup>	10.32	8.01	7.71
Ash <sup>a</sup>	1.78	1.59	0.94
H/C	1.42	1.25	1.08
N/C	0.031	0.050	0.055
S/C	0.009	0.0067	0.0052
O/C	0.104	0.079	0.074
Molecular Weight <sup>b</sup>	1101	461	662

Empirical Formula {  $C_{69.6}H_{98.5}N_{2.2}S_{0.6}O_{7.2}$   $C_{40.6}H_{43.9}N_{2.2}S_{0.2}O_{3.0}$   
 $C_{29.8}H_{37.3}N_{0.5}S_{0.2}O_{2.4}$

- a percent by weight.
- b by VPO in benzene
- c by difference

Table III. Fractional Proton Distribution of Shale Oil Asphaltenes

Proton Type	Bitu	R <sub>425</sub>	R <sub>500</sub>
H <sub>A</sub>	0.046	0.145	0.179
H <sub>α</sub>	0.204	0.337	0.402
H <sub>B</sub>	0.525	0.389	0.330
H <sub>γ</sub>	0.225	0.129	0.089

Table II. IR Absorbance of Shale Oil Asphaltenes

Wavenumber (cm <sup>-1</sup> )	Bitu	R <sub>425</sub>	R <sub>500</sub>
3600	0.06	0.10	0.07
3460	0.08	0.20	0.24
3180	0.10	0.15	0.18
2925	1.76	1.19	0.91
2860	0.88	0.64	0.54
1700	0.61	0.59	0.38
1650	0.34	0.54	0.61
1600	0.30	0.52	0.63
1440	0.53	0.54	0.54
1375	0.35	0.42	0.55

Table IV. Average Structural Parameters of Shale Oil Asphaltenes

	Bitu	R <sub>425</sub>	R <sub>500</sub>
f <sub>a</sub>	0.38	0.49	0.57
f <sub>a</sub> (C) <sup>a</sup>	0.24	0.51	0.60
σ	0.69	0.54	0.53
n	4.31	2.41	1.97
$\frac{H_{ar}}{C_{ar}}$	0.56	0.80	0.71
R <sub>A</sub>	6.8	2.5	4.4
R <sub>A</sub> (C) <sup>a</sup>	4.7	2.5	4.5

<sup>a</sup> Calculated according to the aromaticity determined by <sup>13</sup>C NMR.

Table V. Fractional Carbon Distribution of Shale Oil Asphaltenes

Assignments	Chemical Shift	Bitu		R <sub>500</sub>	
		% of total carbon	% of aliphatic carbon	% of total carbon	% of aliphatic carbon
Carbonyl	168-210	1.3		--	
Aromatic C-O	148-168	1.1		2.8	
Mainly aromatic C-C	129.5-148	10.3		20.8	
Mainly aromatic C-H	100-129.5	12.7		36.0	
CH in alkyl groups (except iso-alkyls) and naphthenic rings. Ring joining CH <sub>2</sub> . CH <sub>2</sub> in alkyl groups adjacent to CH.	37-60	17.3	23.2	6.7	16.6
CH <sub>2</sub> in alkyl groups not adjacent to CH (except some α CH <sub>2</sub> and CH <sub>2</sub> adjacent to terminal CH <sub>3</sub> in alkyl groups >C <sub>4</sub> ). CH <sub>2</sub> in ring joining ethylene groups α CH <sub>2</sub> and CH. β CH in hydroaromatic rings. Naphthenic CH <sub>2</sub> .	27.5-37	33.9	45.4	12.8	31.6
Naphthenic CH <sub>2</sub> . Shielded α CH <sub>2</sub> . β CH <sub>2</sub> in indan and propyl group β CH <sub>3</sub> in iso-propyl.	24-27.5	8.0	10.7	3.3	8.1
CH <sub>2</sub> adjacent to terminal CH <sub>3</sub> in alkyl groups > C <sub>4</sub> . β CH <sub>2</sub> in unsubstituted tetralin structures. CH <sub>3</sub> on hydroaromatic and naphthenic rings.	22.5-24	2.9	3.9	1.3	3.1
α CH <sub>3</sub> not shielded by any adjacent rings or groups.	20.5-22.5	4.5	6.0	3.2	7.8
α CH <sub>3</sub> shielded by 1 adjacent ring or group.	18-20.5	4.0	5.4	3.7	9.1
β CH <sub>3</sub> in ethyl groups.	15-18	2.7	3.6	3.3	8.1
α CH <sub>3</sub> shielded by 2 adjacent rings or groups CH <sub>3</sub> γ or further from an aromatic ring.	9-15	1.3	1.7	6.3	15.6

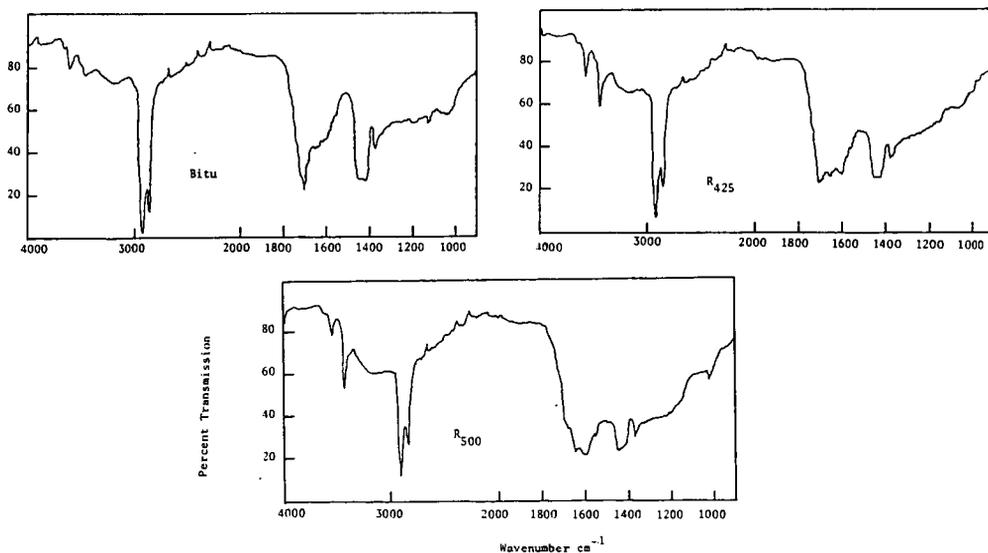


Figure 1. IR Spectra of Shale Oil Asphaltenes

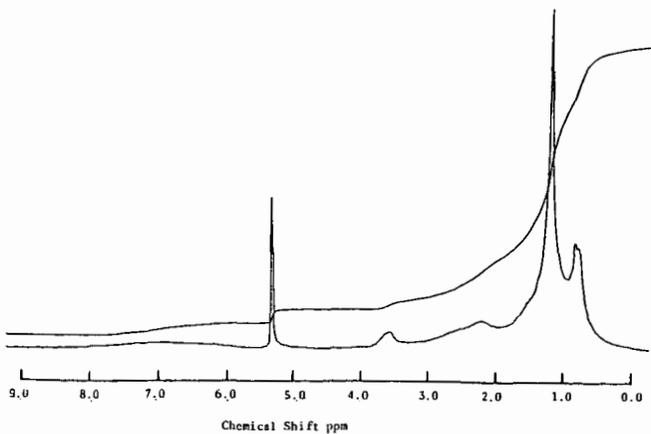


Figure 2.  $^1\text{H}$  NMR Spectrum of Asphaltene From Shale Bitumen (Bitu).

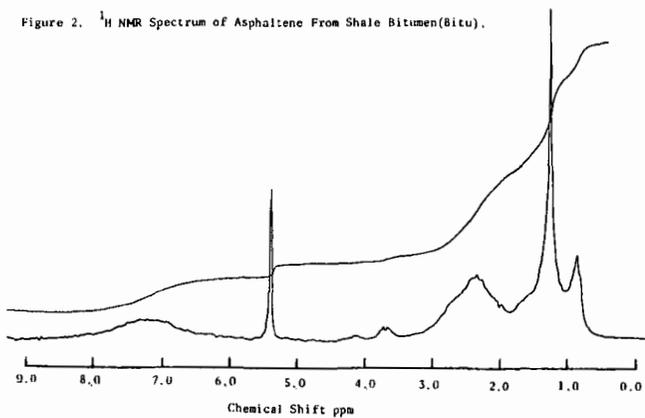


Figure 3.  $^1\text{H}$  NMR Spectrum of Asphaltene From Shale Oil Retorted at  $425^\circ\text{C}$  ( $\text{R}_{425}$ ).

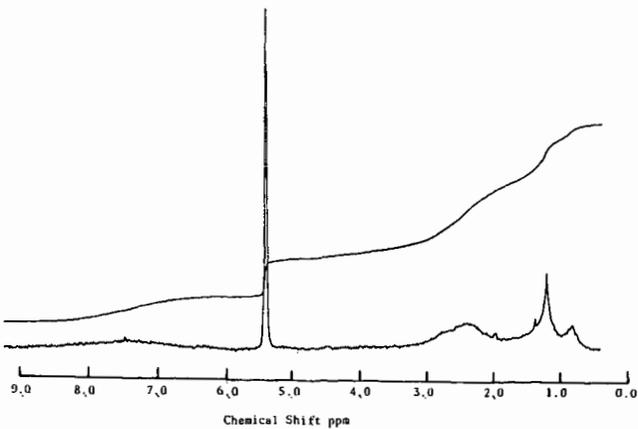


Figure 4.  $^1\text{H}$  NMR Spectrum of Asphaltene From Shale Oil Retorted at  $500^\circ\text{C}$  ( $\text{R}_{500}$ ).

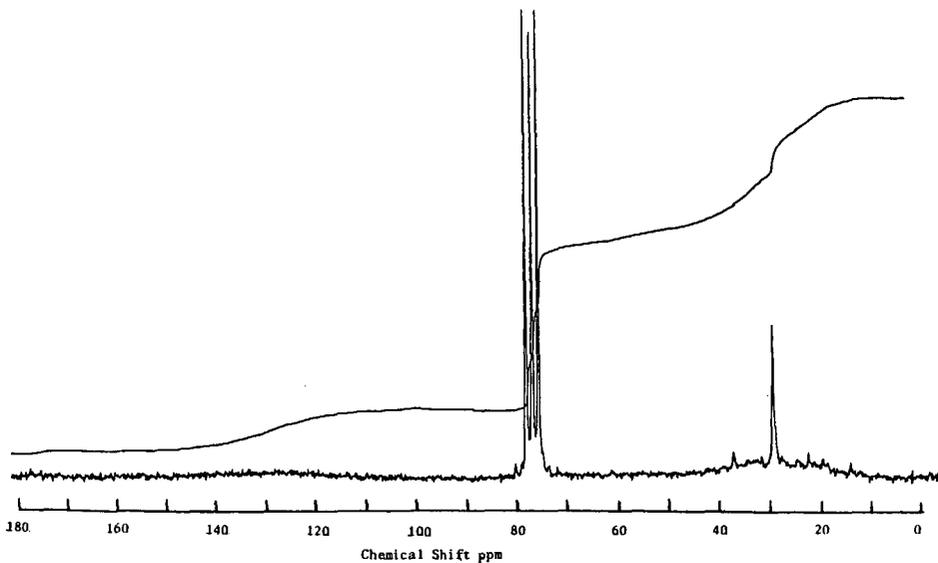


Figure 5.  $^{13}\text{C}$  NMR Spectrum of Asphaltene From Shale Bitumen (Bitu).

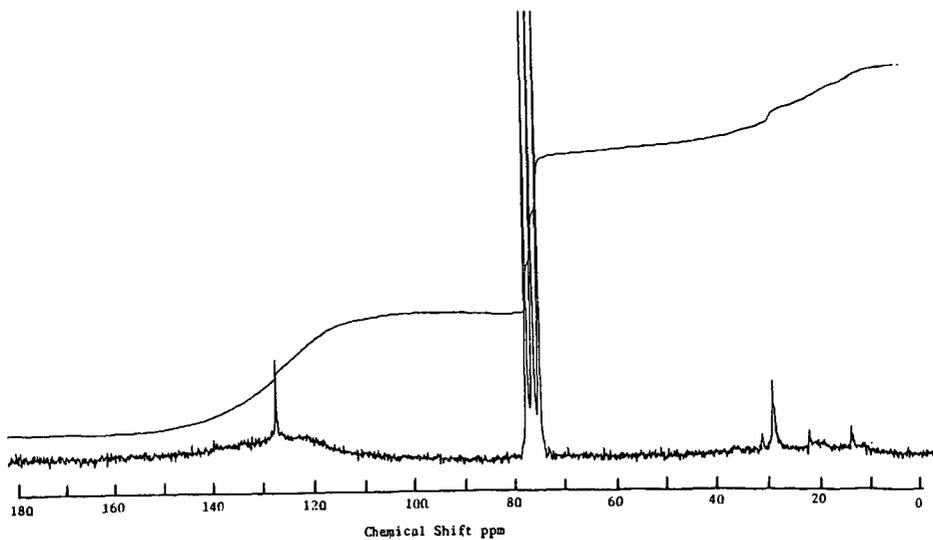


Figure 6.  $^{13}\text{C}$  NMR Spectrum of Asphaltene From Shale Oil Retorted at  $500^\circ\text{C}$  ( $R_{500}$ ).