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NMR AND GC/MS INVESTIGATION OF THE SATURATE AND DISTILLATE
FRACTIONS FROM THE CERRO NEGRO HEAVY PETROLEUM CRUDE

By
Daniel A. Netzel
Frank D. Guffey

August 1987

Work Performed Under Contract No. FC21-83FE60177

For
U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Laramie Project Office
Laramie, Wyoming

By
Western Research Institute
Laramie, Wyoming

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SUMMARY

Six fractions of the Cerro Negro heavy petroleum crude have been evaluated using nuclear magnetic resonance spectroscopy (NMR) and gas chromatography/mass spectrometry (GC/MS). The six fractions include four saturated hydrocarbon distillate fractions distilling above 200°C (200-425°C [392-797°F], 425-550°C [797-1022°F], 550-700°C [1022-1292°F], and >700°C [>1292°F]) and two distillate subfractions of the Cerro Negro petroleum designated as <200°C and >200°C.

The >700°C and 550-700°C saturated hydrocarbon fractions are not suited for analyses by combined GC/MS because their distillation ranges are higher than the upper limit of material that will elute from the gas chromatographic column. None of the material in the >700°C saturated hydrocarbon fraction and only 7% by volume of the 550-700°C saturated hydrocarbon fraction eluted from the column. For this reason, there is not sufficient data for evaluation of these samples by GC/MS.

The ¹H and ¹³C NMR spectral data for the 550-700°C and >700°C saturate fractions indicate that normal and branched alkanes with an average carbon chainlength of C₁₀ are present in these saturate fractions but must be bonded to a larger molecular moiety based upon mass spectral evidence and boiling point considerations. The average molecular structure representation for the 550-700°C saturate fraction is a highly substituted tetracyclic alkane, whereas the >700°C saturate fraction is a highly substituted pentacyclic alkane. At least one carbon chainlength of C>9 is attached to the ring structure for each fraction.

The two remaining saturated hydrocarbon fractions (200-425°C and 425-550°C) were suited for GC/MS evaluation. Normal and branched alkanes were not detected in either of these samples at concentrations of 0.01% by weight. The maximum concentration of normal alkanes that could be present in the 200-425°C and 425-550°C saturated hydrocarbon fractions was estimated using previously determined simulated distillation results and the detection limit of normal alkanes for the GC/MS method; the concentrations were 0.22% and 0.11% by weight, respectively.

NMR data for the 200-425°C saturate fraction give no indication of normal alkanes with carbon chainlengths greater than nine. Branched alkanes possibly of the isoprenoid-like structure are present. The average molecular structural representation from NMR data is an alkyl-substituted dicyclic alkane.

The average molecular structural representation from NMR data for the 425-550°C saturate fraction is also an alkyl-substituted dicyclic alkane. However, at least one of the alkyl substituents has a carbon chainlength greater than 10 since there is evidence in the ¹³C NMR spectrum for a long carbon chain normal alkane. The branched alkanes evident in the ¹³C NMR spectrum must be substituents on the ring structure as suggested by the mass spectral data in which no non-bonded branch alkanes of any significant concentration are present.

Two distillate subfractions of the Cerro Negro heavy petroleum crude identified as <200°C and >200°C were also evaluated by both NMR and GC/MS. These two fractions were generated by using a spinning band column distillation technique on the 200°C fraction of the Cerro Negro petroleum prepared originally by wall-wiped distillation. Both normal and branched alkanes with carbon number range 7 to 12 were detected in the <200°C fraction of the Cerro Negro petroleum using GC/MS. The concentration of the alkanes was estimated by two methods and was found to be between 1% and 3% by weight. Normal alkanes of carbon number range 12 to 31 were identified in the >200°C fraction of the petroleum. The concentration of the normal alkanes was estimated to be approximately 1% by weight. Branched alkanes were not detected in the >200°C sample at the detection limit of 0.01% by weight.

The conventional ¹H and ¹³C NMR spectra for the two distillate subfractions indicate similar chemical composition. However, the DEPT (Distortionless Enhancement by Polarization Transfer) and QUAT (Quaternary-only Carbon Spectrums) NMR experiments suggest that the >200°C distillate subfraction has a larger proportion of quaternary aromatic carbons due to ring condensation and/or alkyl substitution of the aromatic rings. The >200°C distillate subfraction also has a larger proportion of methylene carbons relative to the <200°C subfraction, which suggests a greater number or size of the cycloalkanes since n-alkanes of C₁₀ or greater are not present in any appreciable amounts.

Average molecular structural parameters cannot be calculated for the two distillate subfractions because both fractions are mixtures of aromatics and aliphatic compounds.

INTRODUCTION

The Cerro Negro petroleum is heavy crude from the Orinoco oil belt of Venezuela. This petroleum is classified as an unconventional heavy crude because there is evidence that it has been biodegraded (Grizzle et al. 1981). It is questionable whether conventional methods of petroleum analysis and refinery processing are adequate for an unconventional, biodegraded petroleum such as Cerro Negro petroleum. For these reasons, a cooperative program between the U.S. Department of Energy and the Ministry of Energy and Mines of Venezuela was initiated in 1980 to study the chemical composition of the Cerro Negro heavy petroleum crude.

The objectives of the total program were to perform a detailed characterization of the petroleum, to modify existing methods or to develop new methods for the analysis of heavy oils, and to relate the composition of the petroleum to heavy oil processing technology. The objective of this study relates to the first objective of the program that is to perform a detailed characterization of the petroleum. In particular, these results report on the spectroscopic investigation of the saturate fractions to determine the presence or absence of normal and branched alkanes.

The question of whether or not normal and branched alkanes are present in this petroleum is important because there are indications that the petroleum has been biodegraded. Biodegraded petroleums normally have significantly lower concentrations of acyclic alkanes than do non-biodegraded petroleums. Analyses of the 200-425°C and 425-550°C saturate hydrocarbon fractions using the ASTM mass spectrometric method D-2786 determined that these fractions contained 11.28% and 6.00% by volume of acyclic alkanes, respectively (Brown et al. 1986). These results may be correct, but the potential problems of using this method require that the results be confirmed by other independent methods of analysis.

The potential errors that may arise when analyzing unconventional petroleums would stem from the assumptions used in the initial development of this method (D-2786). It was developed for data obtained from more conventional, mid-continent petroleums and to account for various interferences. The off-diagonal matrix elements associated with the mathematical reduction of the mass spectrometric data may not be adequate for unconventional petroleums like the biodegraded Cerro Negro heavy petroleum crude. For this reason, the analysis of an unconventional crude using the standard ASTM method of analyses may not accurately reflect the concentration of hydrocarbon types present. It is important, therefore, that accurate analytical data be obtained which can be used in conjunction with other data in making good processing decisions for the Cerro Negro crude.

This report describes the results of applying nuclear magnetic resonance (NMR) and gas chromatographic/mass spectrometric (GC/MS) techniques to the saturate hydrocarbon fractions to determine the presence of acyclic alkanes and compare these results with those from the conventional ASTM mass spectrometric analysis.

EXPERIMENTAL

Sample Preparation

The procedures and results for the preparation of the saturate fractions from the Cerro Negro heavy petroleum crude have been described in detail (Grizzle et al. 1981; Brown et al. 1986), but a summary will be provided here for completeness. The Cerro Negro petroleum crude was distilled into five fractions using a 4-inch, wiped-wall still. The five fractions resulting from this distillation are (1) <200°C, (2) 200-425°C, (3) 425-550°C, (4) 550-700°C, and (5) >700°C. In addition, the <200°C fraction was redistilled using a spinning band column to yield two more well-defined fractions identified as <200°C and >200°C distillate subfractions. These subfractions should not be confused with the <200°C distillate fraction obtained from the 4-inch, wall-wiped distillation which was not analyzed.

Ion exchange chromatography was used to remove the acidic and basic material from each of the distillate fractions distilling above 200°C (200-425°C, 425-550°C, 550-700°C, and >700°C). This separation yielded a neutral fraction for each of the four distillate cuts. The neutral fractions were further separated by preparative HPLC on 2,4-dinitroanilinopropylsilica and silica to yield a saturated hydrocarbon and three aromatic hydrocarbon fractions for each of the distillate fractions distilling above 200°C. The saturated hydrocarbon fractions prepared by HPLC were then analyzed by both NMR and GC/MS.

Nuclear Magnetic Resonance

All samples were prepared with a sample-to-solvent volume ratio of 1:1 using 0.5 mL of CDCl₃ containing ~0.3% TMS. No relaxation reagent was added. The samples were filtered directly into a 5-mm NMR tube using a 5-μ Teflon millipore filter assembly.

A JEOL FX-270 NMR spectrometer with a C/H dual 5-mm probe was used for all experiments. The observed frequencies for ¹H and ¹³C were 269.65 and 67.88 MHz, respectively. Conventional ¹H spectra were obtained using a pulse width of 5 μs (46°), a pulse delay of 20 sec, and a total of 7 transients. Normal ¹³C spectra were obtained using a pulse width of 6 μs (90°), 500 or 700 real transients, 8 dummy transients, a pulse delay of 20 sec, and gated ¹H decoupling to ensure quantitative results.

DEPT (Distortionless Enhancement by Polarization Transfer) and QUAT (Quaternary-only Carbon Spectrum) experiments were performed on the samples using the pulse sequences described by Bendall and Pegg (1983) and Bendall et al. (1982). For both the DEPT and QUAT spectra, the carbon-hydrogen spin coupling constant, J, was set equal to 125 Hz for the saturate hydrocarbon samples and 140 Hz for the <200°C and >200°C distillate subfractions. The ¹H pulse width was set equal to 45°, 90°, and 135° to obtain the three initial DEPT spectra. The 90° ¹H pulse width was obtained at the point where the intensity of the CH₂ resonance of o-ethyltoluene containing the relaxation reagent, Tris (acetylacetonato) chromium (III) [Cr(AcAc)₃], was zero. In both the DEPT

and QUAT experiments, the ^{13}C 90° and 180° pulse widths used were 6 and 12 μsec , respectively. A pulse delay of 10 sec was used in the DEPT experiments. A pulse delay of 20 sec was used in the QUAT experiments to reduce any errors caused by carbon types with long spin-lattice relaxation times. For the saturate and distillate samples, 500 or 700 transients and 8 dummy pulses (to achieve thermal equilibrium) were collected for the DEPT 45° and 135° spectra and the quaternary-only carbon spectra. Twice as many transients were taken to obtain the DEPT 90° spectrum to eliminate a factor of two in the addition and subtraction of the initial DEPT spectra (Bendall and Pegg 1983). All experiments were carried out using 16 K data points over a spectral width of 15 KHz and at a temperature of 24°C .

NMR Methodology for Carbon Type Analysis

Spectral editing of the DEPT and QUAT spectra was performed using the methodology described by Netzel (1987). For completeness of this report, a brief description of the methodology follows. The carbon type subspectra (CH_n) can be obtained from the addition and subtraction of the initial DEPT spectra according to equations 1, 2, and 3 (Bendall and Pegg 1983).

$$\theta_{\text{CH}} = \theta_{90} - x(\theta_{45} + y\theta_{135}) \quad (1)$$

$$\theta_{\text{CH}_2} = \theta_{45} - y\theta_{135} \quad (2)$$

$$\theta_{\text{CH}_3} = \theta_{45} + y\theta_{135} - z\theta_{90} \quad (3)$$

where θ_{45} , θ_{90} , and θ_{135} represent the spectrum obtained when the ^1H pulse width is set to rotate the ^1H spins 45° , 90° , and 135° .

Because of missetting or field inhomogeneity of the ^1H pulse, it was necessary for some samples to correct the initial 90° DEPT spectrum for residual methylene carbons by subtracting the methylene subspectrum (θ_{CH_2}) from θ_{90} before calculating the subspectra of the methine and methyl carbons.

The corrected linear combination of subspectra for the methine and methyl carbons is given in equations 4 and 5, respectively.

$$\theta'_{\text{CH}_3} = (\theta_{90} - a\theta_{\text{CH}_2}) - x'(\theta_{45} + y\theta_{135}) \quad (4)$$

$$\theta'_{\text{CH}_2} = (\theta_{45} + y\theta_{135}) - z'(\theta_{90} - a\theta_{\text{CH}_2}) \quad (5)$$

It was also necessary for some samples to correct the quaternary-only carbon spectrum for residual methylene carbons (Bendall and Pegg 1983) by subtracting the DEPT θ_{CH_2} spectrum from the quaternary-only carbon spectrum, θ_{QUAT} (Equation 6).

$$\theta'_{\text{QUAT}} = \theta_{\text{QUAT}} - b\theta_{\text{CH}_2} \quad (6)$$

The coefficients a, b, y, x', and z' are determined experimentally.

Although the DEPT method provides quantitative data for methyl, methylene, and methine carbons, it does not provide any quantitative data on the quaternary carbons. The integrated, edited DEPT spectra for the three carbon types cannot be compared to the integrated quaternary-only carbon spectrum because the methods to obtain the spectra differed in signal enhancement efficiencies. However, it is possible to relate quantitatively through equation 7 the integrated spectra obtained by the two techniques to obtain a complete quantitative carbon type analysis.

$$\sum I\theta_{\text{CH}_n} = k I [\theta_N - \theta'_{\text{QUAT}}] \quad (7)$$

where $\sum I\theta_{\text{CH}_n}$ is the sum of the integrated values of the carbon types obtained from the DEPT subspectra and $I[\theta_N - \theta'_{\text{QUAT}}]$ is the integrated value from the spectrum obtained from the computer subtraction of the adjusted quaternary-only carbon spectrum from the ^{13}C normal spectrum. All integration values are referenced to the integration value of the normal ^{13}C spectrum taking into account the differences in gain settings between spectra.

Equation 7 is solved for the proportionality constant k. Once k is determined, the fraction of carbon types, f_n^C , in a sample can be determined using equations 8 through 10.

$$k I \theta_{\text{QUAT}} = k I \theta_C \quad (8)$$

$$k I \theta_C + I \theta_{\text{CH}} + I \theta_{\text{CH}_2} + I \theta_{\text{CH}_3} = I \theta_{\text{Total}} \quad (9)$$

$$f_n^C = \frac{I \theta_n}{I \theta_{\text{Total}}} \quad (10)$$

where $I \theta_n$ is the integrated value for the specific carbon type spectrum.

Gas Chromatography/Mass Spectrometry

GC/MS analyses were performed on the saturated hydrocarbon fractions distilling above 200°C and the <200°C and >200°C petroleum distillate subfractions produced by spinning-band distillation. The <200°C distillate subfraction was also analyzed to determine the hydrocarbon compound types using the WRI proprietary GC/MS hydrocarbon compound type analysis method. The method was developed for the analysis of distillate fuels and is based on sensitivity factors for

selected ions for each compound class of hydrocarbons. The instrumental conditions used for the GC/MS analysis are given in Table 1.

Table 1. Gas Chromatographic/Mass Spectrometric Conditions Used for the Evaluation of the Saturate and Distillate Fractions from the Cerro Negro Heavy Petroleum Crude

<u>Mass Spectrometer (Hewlett-Packard 5985B)</u>	
Ionization mode	electron impact
Electron voltage	70 volts
Ion source temperature	200°C
Electron multiplier voltage	1600 volts
Mass range scanned	50-500 amu
Scan rate	1.3 seconds/decade
Resolution	1/1000

<u>Gas Chromatograph (Hewlett-Packard 5840)</u>	
Column (25m x 0.20mm [ID] x 25m)	methyl silicone (5%), 0.33 μ m thickness
Oven program	50-275°C (3°/min)
Carrier gas	He
Flow rate	0.75 mL/min
Injection temperature	275°C
Sample size	1 μ L
Split ratio	100:1

GC/MS Methodology for Quantitative Analysis

Each of the six samples was analyzed with the addition of an internal spike. The spike used for this analysis was a shale oil neutral fraction. The shale oil was produced in the Western Research Institute (WRI) low void volume retort (Guffey and McLendon 1984). The neutral fraction was prepared from the raw shale oil using the method of Jackson et al. (1978). This standard was selected as the spike for this study because it has been well characterized and contains all of the

normal alkanes and many of the branched alkanes expected to be present in a petroleum.

The GC/MS data from the samples were evaluated to determine the presence of alkanes by mapping selected ions that are representative of normal and branched alkanes. The ions selected for this effort were $m/z=57$, 71, 85, and 99. These ions represent the major fragment ions of normal and branched alkanes. The four fragment ions ($m/z=57$, 71, 85, and 99) are considered to arise from fragmentation of an alkane only if the maximum of each peak in the selected ion current chromatograms ($m/z=57$, 71, 85, and 99) does not vary by more than two mass spectral scans. The sample-plus-spike experiments were evaluated in the same manner, and the results were compared with the sample results. The intensity of alkanes present in the sample increases with the addition of the spike and confirms the detection of the individual alkanes. An alkane detected by this method can be identified by (a) interpretation of the mass spectra if the alkane is present in high enough concentration to produce a reliable mass spectrum and the mass spectrum is free of interferences from co-eluting compounds or (b) by comparison of gas chromatographic retention time with retention times of known alkanes.

The detection limit as defined by the GC/MS method is the concentration where the presence of an alkane can be detected in a sample. The lower detection limit of the method must be determined so that a limit of the concentration of alkanes in the samples can be established. The detection limit of this method was determined by performing a series of experiments using serial dilutions of n-hexadecane in n-hexane and evaluating the ion responses. Normal hexadecane was chosen as the alkane for determination of the detection limit because it falls in approximately the mid-molecular weight range of the method.

The detection limit of the GC/MS method for four selected ions of n-hexadecane ($m/z=57$, 71, 85, and 99) is given in Table 2. Column 1 of Table 2 lists the concentration of n-hexadecane in n-hexane that was prepared and serially diluted. Column 2, the quantity of n-hexadecane injected on the column, is the weight of n-hexadecane placed on the column by injecting 1 μ L of solution with a 100:1 split ratio. The estimated concentration of n-hexadecane in a sample, column 3, is the weight percentage of n-hexadecane that would be found in a sample assuming a specific gravity of 0.8. Column 4 lists the areas of the reconstructed ion current chromatogram peaks of each ion in arbitrary units. The four selected ions could not be detected above the baseline noise levels below a concentration of 0.1 mg/mL. Based on this observation, the detection limit for n-hexadecane using this method is 0.1 mg/mL (0.01% by weight).

The detection limit for n-hexadecane can be extended to other normal alkanes that are in the range of molecular weights accommodated by the method. The relative percentages of the total ionization represented by the four ions used for alkane detection ($m/z=57$, 71, 85, and 99) for normal alkanes of carbon numbers between 10 and 30 are provided in Table 3 (Stenhagen et al. 1969). The relative percentages

do vary but have a mean value of 35.2% with a standard deviation from the mean of 2.7. The value of the percentage of total ionization for n-hexadecane (34.9%) falls within the limits of the standard deviation. Because of the consistency of the relative percentages of the total ionization, as demonstrated by the low standard deviation value and the value for n-hexadecane falling within one standard deviation of the

Table 2. Serial Dilution of n-Hexadecane to Determine the Detection Limit of the GC/MS Method

Concentration of n-hexadecane in standard solution (mg/mL)	Quantity of n-hexadecane injected on column (nanograms) ^a	Estimated concentration of n-hexadecane in a sample (wt %) ^b	Ion areas ^c (arbitrary units)				
			57	71	85	99	Sum
10.0	100	1.25	1090	684	525	249	2548
5.0	50	0.63	681	369	309	144	1503
1.0	10	0.13	228	110	84	38	460
0.1	1	0.01	28	21	8	5	62

^aWeight of n-hexadecane placed on the column by injecting 1 μ L of the solution with a 100:1 split ratio

^bWeight percent of n-hexadecane that would be found in a sample assuming a specific gravity of 0.8

^cAreas of the reconstructed ion current chromatogram peaks

mean, it is felt that the detection limit determined for n-hexadecane is applicable to other normal alkanes. Data are not available for the large number of branched alkanes that would be included in this molecular weight range. The detection limit for these compounds is probably comparable to that of the normal alkanes because the selected ions used for the detection method still represent a significant portion of the total ionization of branched alkanes in this carbon number range. This is particularly true for the higher molecular weight branched alkanes (carbon number greater than 12).

The detection limit for this method is below the concentration where a reliable mass spectrum can be recorded for qualitative identification of the alkane. In a well-separated sample, the lower concentration where a reliable mass spectrum can be recorded for n-hexadecane is 1.0 mg/mL. At concentrations below this level, identification must be performed using other data such as GC retention time of the eluting components.

Table 3. Relative Percentage of Total Ionization of the Selected Ions for Normal Alkanes^a

Normal Alkane Carbon Number	Mass (AMU)	Relative Percentage of Total Ionization (57 + 71 + 85 + 99)
10	142	29.2
11	156	29.9
12	170	32.0
13	184	34.9
14	198	38.8
15	212	39.5
16	226	34.9
17	240	36.5
18	254	33.6
19	268	N.A. ^b
20	282	38.3
21	296	36.9
22	310	35.2
23	324	35.9
24	338	34.6
25	352	36.4
26	366	N.A.
27	380	35.8
28	394	37.0
29	408	34.3

^aFrom: Atlas of Mass Spectral Data, Stenhagen, E., S. Abrahamsson, and F. W. McLafferty, eds.; Interscience Publishers: New York, 1969

^bN.A. = Not Available

RESULTS AND DISCUSSION

Saturate Fractions of the Cerro Negro Heavy Petroleum Crude

Figures 1 and 2 are the ¹H and ¹³C spectra, respectively, for the four saturate fractions. A small amount of monoaromatic is evident in both the ¹H spectrum (7.32 ppm) and ¹³C spectrum (128.2 ppm) for the 550-700°C and >700°C saturate fractions. The chemical shift data suggest that the monoaromatic is benzene, which possibly evolved from the separation scheme used to isolate the saturate fractions.

The ¹H resonances (Figure 1) between 0.8 and 0.9 ppm and at 1.25 ppm are due to methyl and methylene groups, respectively, for normal and branched alkanes. The broad resonances between 1.4 and 2.0 ppm are mostly associated with methine and cyclic methylene hydrogens. It is interesting to note that as the distillate temperature of the saturate fraction increases (increase in average molecular weight), the ratio of

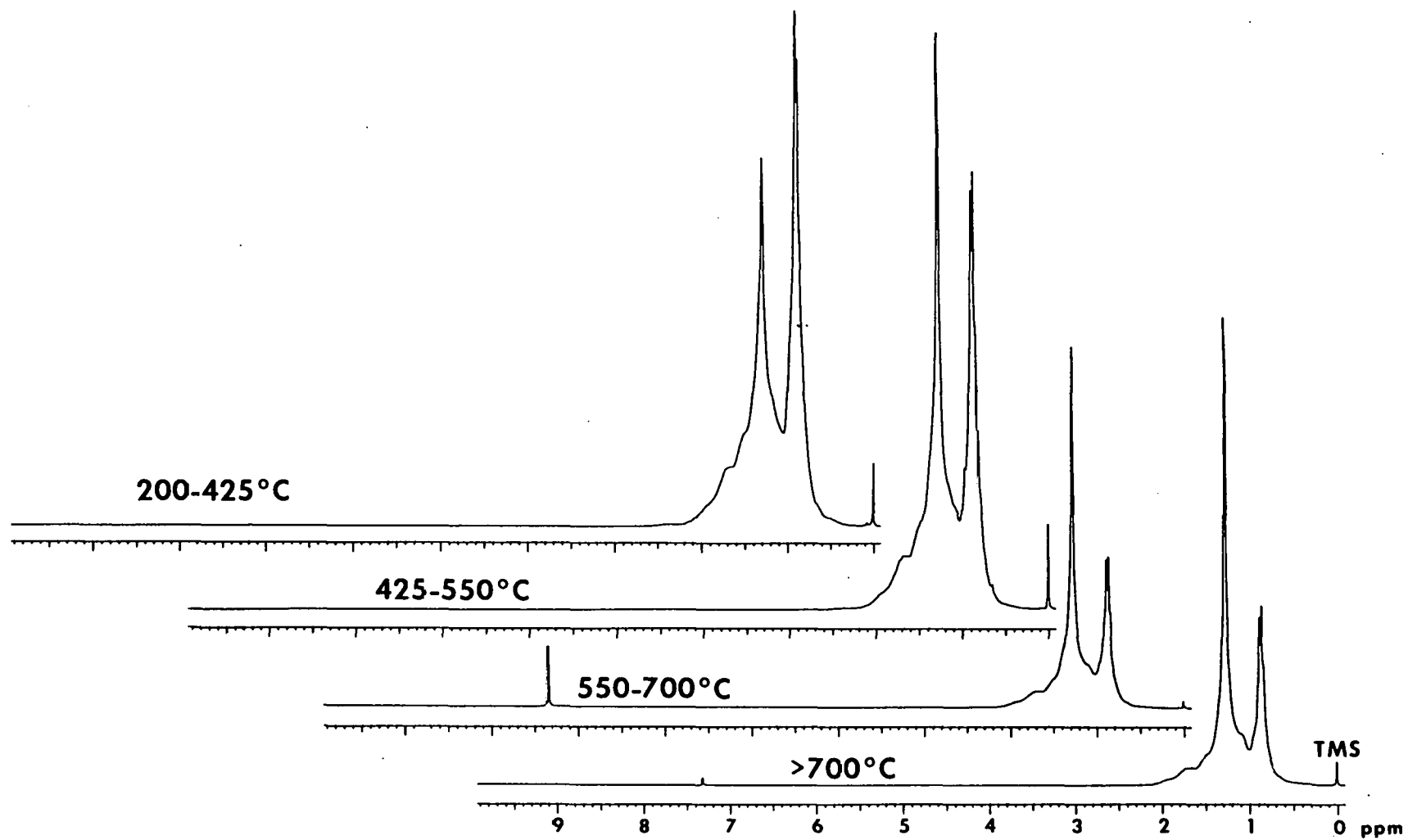


Figure 1. ^1H NMR Spectra of the Four Saturate Fractions from the Cerro Negro Heavy Petroleum Crude

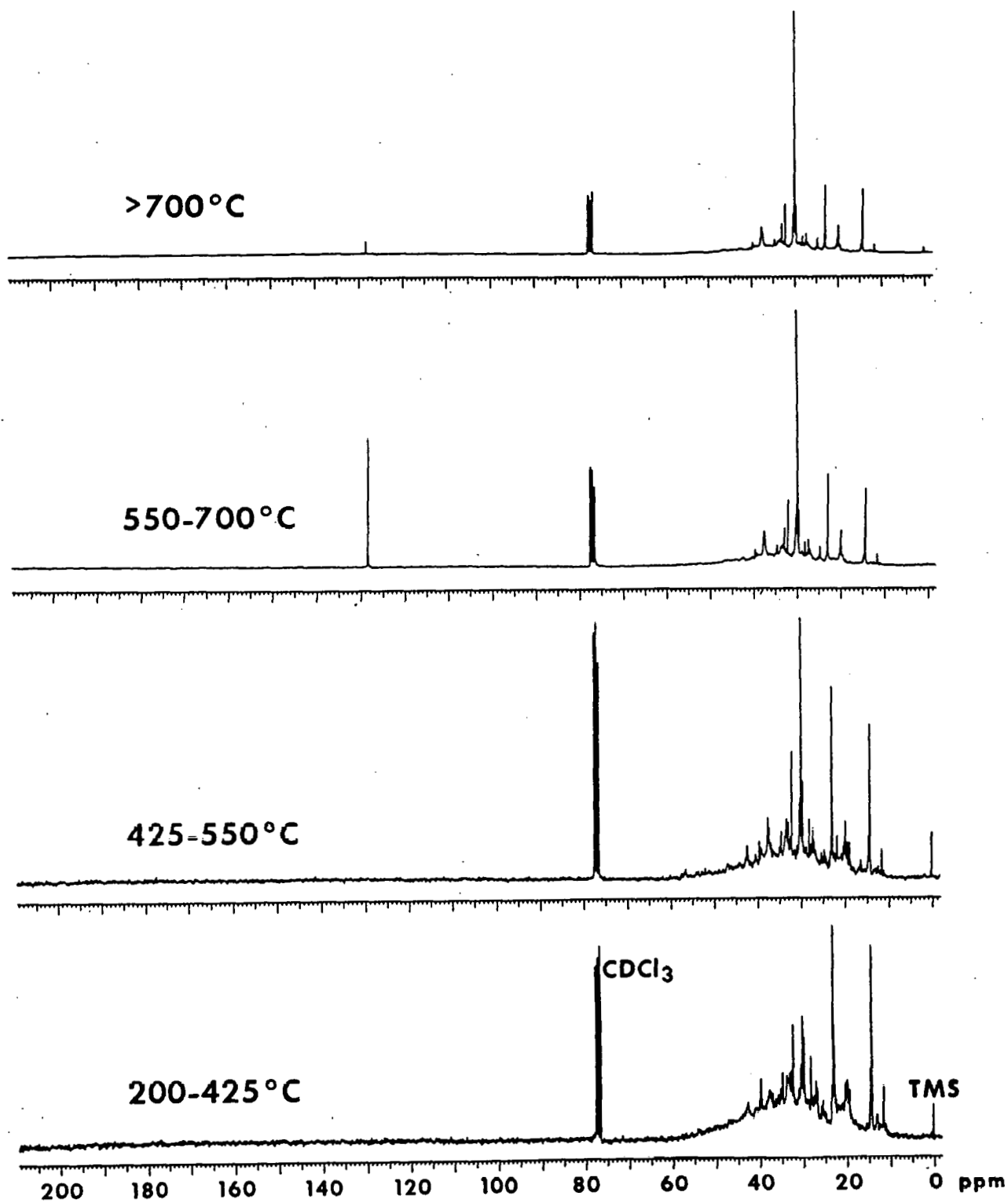


Figure 2. ^{13}C NMR Spectra of the Four Saturate Fractions from the Cerro Negro Heavy Petroleum Crude

methyl to methylene hydrogens decreases. This decrease suggests an increase in the number of saturate rings and/or the normal alkane carbon chainlength with a corresponding decrease in branched alkanes. These normal and branched alkanes may exist either separately or bonded to another molecular moiety.

Many of the resonances in the ^{13}C NMR spectra (Figure 2) can be identified as carbons belonging to normal alkanes (14, 23, 32, 30, and 29.5 ppm) and branched alkanes of the isoprenoid class of compounds. It is not surprising that the ^{13}C spectra also show an increase in normal alkane moiety relative to branched alkanes with an increase in the distillation temperature.

The direct identification of cycloalkanes in the ^{13}C spectra of the saturate fractions is difficult to ascertain. Some information about the average number of rings and branch sites of a cycloalkane can be obtained from ^{13}C subspectral analysis of the saturate fractions. The normal ^{13}C and carbon-type (CH_n , $n=0-3$) spectra for the 200-425°C saturate fraction appear in Figure 3. This set of spectra is typical of the DEPT/QUAT spectra obtained for each of the four saturate fractions.

Integration of each carbon-type spectrum yields the fractional amount of carbon type in the sample. The C and H atom percent for the carbon types for each of the saturate fractions is listed in Table 4. The atom percent of hydrogen listed for each fraction was calculated from the ^{13}C data and normalized to 100. The average molecular parameters for the four saturate fractions are listed in Table 5. The H/C ratios were obtained from the ^{13}C data and from conventional elemental analysis. The agreement of the ratios obtained from the two techniques is good and, thus, validates the carbon-type analysis by NMR.

The average molecular weight was obtained on each of the four distillates before fractionation (Brown et al. 1986). However, as a first approximation this value was used to calculate average molecular structural parameters for the four saturate fractions from the NMR carbon type data. The average number of carbon atoms per molecule (N_C) was calculated from the fraction of carbon type, the average molecular weight, and the molecular weight of the carbon type.

The average number of branching sites (N_B), branches (N_B), and saturate rings (N_R) per molecule were obtained using equations 1 to 3 (Cookson and Smith 1985).

$$BS = N_C \{C + CH\} \quad (1)$$

$$N_B = N_C \{2C + CH\} \quad (2)$$

$$N_R = 0.5N_C \{2C + CH - CH_3\} + 1 \quad (3)$$

C, CH, and CH_3 are the fractions of carbon atoms present as C, CH, and CH_3 groups, respectively.

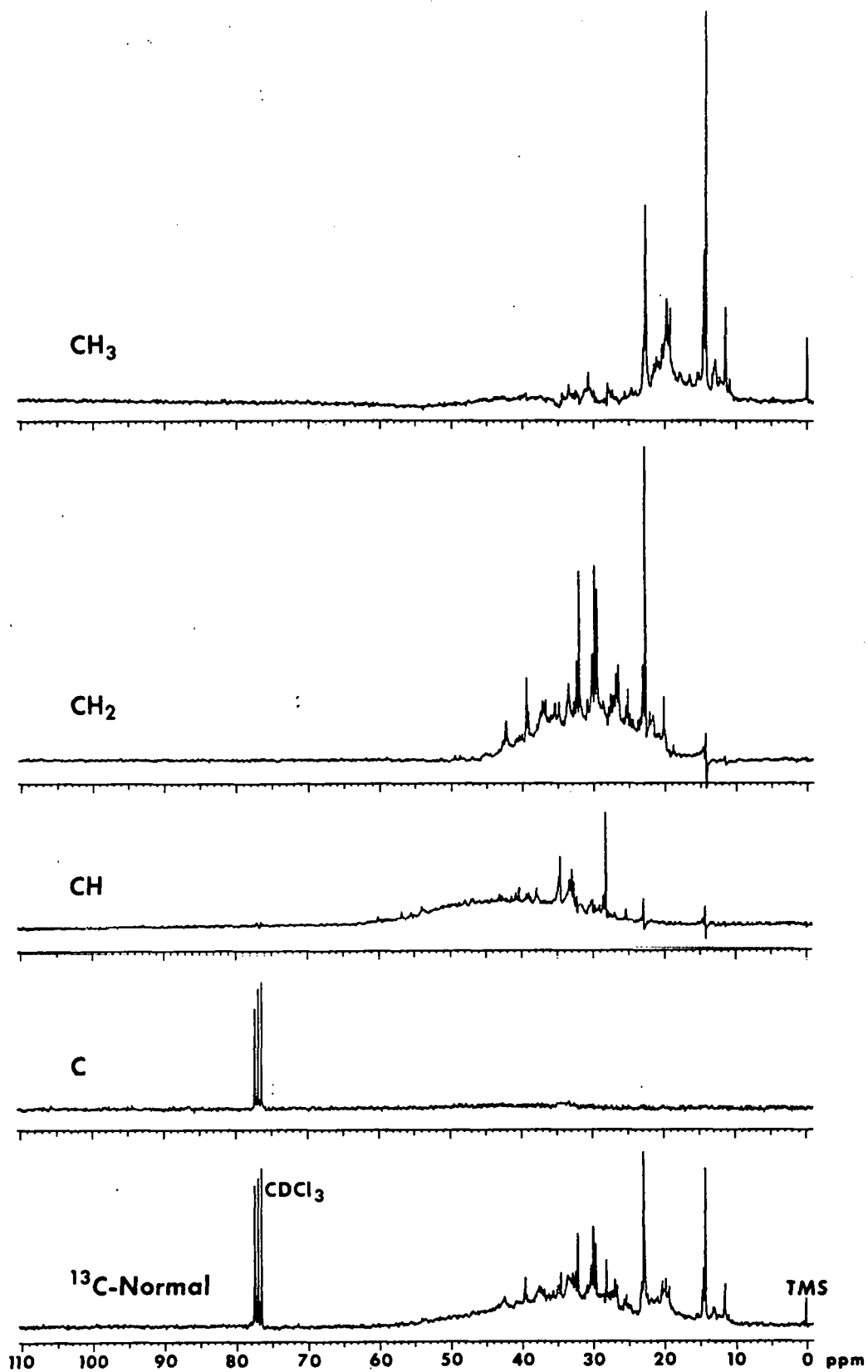


Figure 3. The Normal ^{13}C NMR Spectrum and Carbon Type Spectra for the 200-425°C Saturate Fraction from the Cerro Negro Heavy Petroleum Crude

Table 4. Carbon and Hydrogen Type Distributions for the Saturate Fractions from the Cerro Negro Heavy Petroleum Crude

Carbon Type	Saturate Fractions								
	200-425°C		425-550°C		550-700°C		>700°C+		
	C (atom %)	H (atom %)	C (atom %)	H (atom %)	C (atom %)	H (atom %)	C (atom %)	H (atom %)	
C									
Aromatic	-	-	-	-	-	-	-	-	-
Aliphatic	5.2	-	3.5	-	1.0	-	0.0	-	
CH									
Aromatic									
Aliphatic	28.5	15.4	25.4	13.3	29.1	15.8	27.1	14.4	
CH ₂	42.5	46.0	47.7	49.9	54.4	59.0	57.3	60.7	
CH ₃	23.8	38.7	23.5	36.8	15.5	25.3	15.6	24.9	

Table 5. Average Molecular Structural Parameters for the Saturate Fractions from the Cerro Negro Heavy Petroleum Crude

<u>Structural Parameter</u>	<u>Saturate Fractions</u>			
	<u>200-425°C</u>	<u>425-550°C</u>	<u>550-700°C</u>	<u>>700°C</u>
H/C Ratio	1.85(1.88) ¹	1.91(1.84)	1.84(1.87)	1.89(1.88)
Average Molecular Weight (MW _A)	253 ¹	404	517	991
Average number of Carbon atoms per molecule (N _C)	19.1(19) ²	29.2(29)	37.4(36)	71.5(71)
Average number of branching sites per molecule (BS)	6.4(6)	8.4(8)	11.3(11)	19.4(19)
Average number of branches per molecule (N _B)	7.4(7)	9.5(9)	11.6(11)	19.4(19)
Average number of rings per molecule (N _R)	2.4(2)	2.3(2)	3.9(4)	5.1(5)
Average number of Quaternary Carbons per molecule	1.1(1)	1.2(1)	0.4(0)	0.0(0)
Average number of Methine Carbons per molecule	5.8(5)	7.9(7)	11.6(11)	20.7(19)
Average number of Methylene Carbons per molecule	8.0(8)	13.8(14)	20.1(20)	40.6(41)
Average number of Methyl Carbons per molecule	4.2(5)	6.3(7)	5.3(5)	10.3(11)

¹H/C ratios in parentheses and Average Molecular Weight Data from Brown et al. 1986

²Values in parentheses used to construct Average Molecule

A representation of the molecular structural data given in Table 5 for each of the four saturate fractions is illustrated in Figure 4. These average molecules do not (or may not) exist in the saturate fractions but are presented so the reader can visualize the results of the NMR, average molecular weight, and boiling range data.

200-425°C Saturate Hydrocarbon Fraction

The results of the simulated distillation analysis of the 200-425°C saturated hydrocarbon fraction indicate that the total sample distills below 482°C, which is the upper limit of the distillation temperature for the GC/MS method. Thus, the sample is completely eluted from the gas chromatographic column during the GC/MS experiment.

The GC/MS results of the sample and the sample-plus-spike indicated that neither normal nor branched alkanes were present in this saturated hydrocarbon fraction above 1.0% by weight. Based upon the distillation temperature, the normal alkane carbon number range for the alkanes in this sample would be 12 to 33. Using this information and the detection limit of the method, the estimated concentration of normal alkanes in this fraction is 0.22% by weight. Brown et al. (1986) used the ASTM mass spectrometric method D-2786 to determine that this sample contains 11.28% by volume or about 9% by weight of acyclic alkanes (assuming a specific gravity of 0.8). This value is significantly larger than that determined by the GC/MS method.

The most likely cause of the difference in the values is believed to be the inadequacies of the ASTM method D-2786 for analyzing samples from unconventional petroleums.

The normal ^{13}C NMR spectrum of the 200-425°C saturate fraction shown in Figure 2 does not show the characteristic five-line pattern of n-alkanes with a carbon chainlength greater than 10 carbons. Normal alkanes with a carbon number less than 10 may be present either alone or bonded to another molecular moiety.

Reduction of the ^{13}C DEPT/QUAT spectral data suggests that the average molecular structure is a molecule containing 19 carbons, with 2 saturate rings, 6 branch sites, and 7 branches (Table 5). A correlation of the methyl ^{13}C chemical shift data of this sample with model compounds suggests that two branch sites and three branches are due to a molecular configuration such as found in 1,1,2 and/or 1,1,3-trimethylcyclohexane. The remaining methyl and methylene carbons are combined to give a hypothetical molecular structure as shown in Figure 4. Brown et al. (1986) had reported that cycloalkanes with 1 to 4 rings are present in the 200-425°C saturate fraction in which 32% by volume of the fraction is composed of dicycloalkanes. Monocycloalkanes and tricycloalkanes are almost equally distributed and make up 43% by volume of the fraction; 14% by volume of the sample is made up of tetracycloalkanes. The weighted average ring number per molecule was calculated (Netzel et al. 1981) for the saturate fraction from the data given by Brown et al. (1986) to be 2.7. This value compares favorably with the NMR value of 2.4 given in Table 4. Thus, the distribution of cycloalkanes as determined by Brown et al. (1986) is exactly what is represented by the average structure as computed from NMR data.

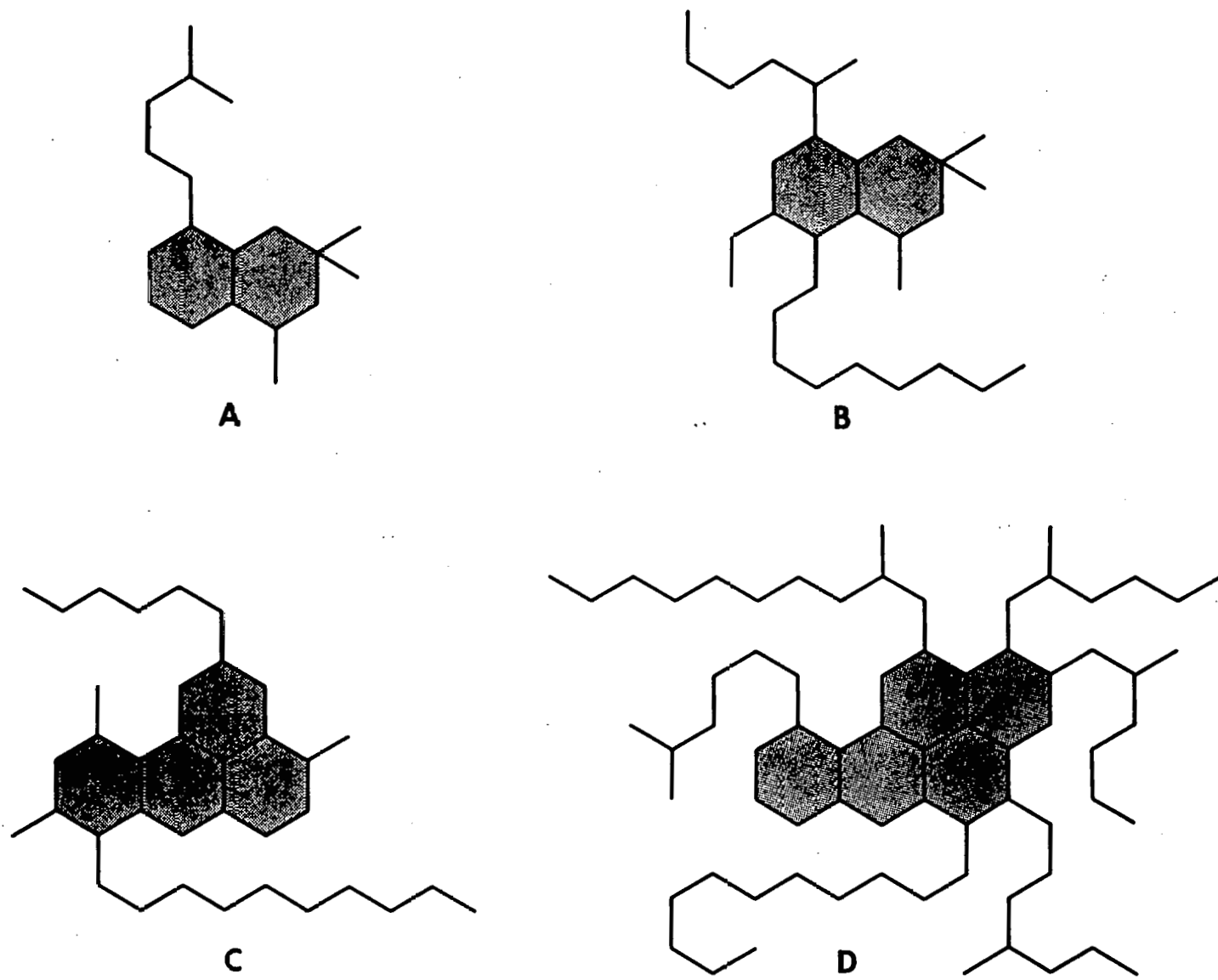


Figure 4. Molecular Structural Representation of the NMR and Molecular Weight Data for the Four Saturate Fractions from the Cerro Negro Heavy Petroleum Crude: (A) 200-425°C, (B) 425-550°C, (C) 550-700°C, and (D) >700°C

425-550°C Saturate Hydrocarbon Fraction

As calculated from the results of the simulated distillation analysis by Brown et al. (1986), only 68% by volume of this sample distills below 482°C. The carbon number range of normal alkanes that would be expected in this portion of the sample is 23 to 33. Using this information and the detection limit of the method, the maximum concentration of normal alkanes that can be present in the sample is 0.11% by weight. The concentration of the branched alkanes can not be estimated as was discussed in the experimental section.

The GC/MS data from both the sample and sample-plus-spike experiments indicated that no normal or branched alkanes are present at or above the detection limit of the method. However, the concentration of acyclic alkanes in the 425-550°C saturate hydrocarbon fraction was determined by Brown et al. (1986) using the ASTM spectrometric method D-2786. The results of their analysis gave a total acyclic alkane concentration of 6.0% by volume. If a specific gravity of 0.8 is assumed for the sample, the concentration of acyclic alkanes by weight is 4.8%. This value is considerably greater than the value determined by GC/MS evaluation of this sample (<0.11% by weight).

The difference in the two mass spectral results can possibly arise from three different sources. The first cause is that the alkanes are concentrated in the portion of the sample that distills above 482°C. This is probably unlikely since hydrocarbons in fossil fuels occur as homologous series, and the lower members of the alkane homologous series should be detectable in the first 68% by volume of material that is suitable for analysis by the GC/MS method.

A second possible cause is that branched alkanes could be present in the sample at concentrations below the detectable limit of the GC/MS method, but a significant number of isomers is present to make up this concentration. If a normal distribution of the sample is assumed, then the number of branched alkanes required to be in the sample below the detection limit required to compose 4.8% by weight of the sample as alkanes can be estimated. An estimation of the number of branched alkanes present at the detection limit is 450. For a normal distribution of the distillate range of the samples, the alkane carbon number range would be expected to be 23 to 40 or a total of 16 carbon numbers. This would imply that, on the average, there would be 28 branched alkanes per carbon number. This number of branched alkanes per carbon number appears unlikely since the branched alkanes normally found in fossil fuels can be related to biologically formed compounds that primarily contain methyl branches in a regular frequency such as the terpenoids. For a 40 carbon terpenoid, there will only be 5 methyl branches in the regular pattern (isoprene units). For this reason it appears unlikely that an inordinately large number of branched alkanes exists in the sample to cause the difference in the two values for acyclic alkanes determined in this sample.

The third possible consideration is that the ASTM method D-2786 is not adequate for the evaluation of a petroleum such as the Cerro Negro heavy petroleum crude. Evaluation of the results that are currently

available indicates that this is the most likely cause of the differences in the values of acyclic alkanes determined by the GC/MS evaluation and the ASTM method D-2786. This inadequacy was the reason for investigating these samples using NMR and the GC/MS methods, and it appears to be a legitimate concern.

The ^{13}C NMR spectrum of the 425-550°C fraction (Figure 2) shows the presence of five resonance characteristics of n-alkanes with a carbon chainlength greater than C_{10} . Assuming that the n-alkanes are not bonded to any other larger molecular moiety, the average n-alkane carbon chainlength is calculated from the integration of these resonances to be C_{11} (Netzel and Hunter 1981). A normal C_{11} alkane has a boiling point of 196°C. This value is much lower than the distillate temperature range of 425-550°C for this fraction. Thus, it is concluded that the n-alkane is a substituent of a larger molecular moiety. The NMR data agree with the GC/MS data that little, if any, free n-alkanes are present in this fraction.

Reduction of the ^{13}C DEPT/QUAT spectral data suggests that the average molecular structure is a molecule containing 29 carbons, with two saturate rings, eight branch sites, and nine branches (Table 5). As was noted for the 200-425°C saturate hydrocarbon fraction, there is also evidence from the methyl ^{13}C chemical shift data for 1,1,2 and 1,1,3-trimethylcyclohexane molecular configuration in the 425-550°C saturate fraction. The remaining methyl and methylene carbons are combined to provide a hypothetical molecular structure as shown in Figure 4. Since the ^{13}C spectrum shows the characteristic five resonances for n-alkanes but was shown not to exist in the free form, a straight-chain alkane of C_9 was attached to one of the saturate rings. The carbon chainlength was calculated from the integration of the spectrum assuming that the resonance at 14 ppm was equal to one methyl carbon instead of two as would be the case if the alkane was not bound to the ring structure.

Brown et al. (1986) had reported that cycloalkanes with one to six rings are present in the 425-550°C fraction. From their data the weighted average number of rings per molecule was calculated to be 3.2 (Netzel et al. 1981). The number of saturate rings per molecule calculated from the NMR data was found to be 2.3 (Table 5).

The NMR and the ASTM mass spectrometric D-2786 methods provide essentially the same results for average number of saturate rings per molecule for both the 200-425°C and 425-550°C saturate fractions. The results do not agree on the presence of acyclic alkanes. However, the NMR method results agree with the GC/MS results in that non-bonded, straight-chain alkanes are not present in either the 200-425°C or the 425-550°C fractions.

550-700°C Saturate Hydrocarbon Fraction

The results of the simulated distillation analysis by Brown et al. (1986) indicate that less than 7% by volume of this sample distills below 482°C; therefore, little information can be obtained using the GC/MS method.

However, the GC/MS experiments were performed on the sample, and the data from both the sample and sample-plus-spike experiments were evaluated to determine whether alkanes were present in the 7% by volume fraction. Neither normal nor branched alkanes were detected in the sample analyzed by this method. The distillation range of the material eluting from the gas chromatographic column covered a normal alkane carbon number range of 19 to 33. The maximum concentration of normal alkanes that could be present in 7% by volume of the sample analyzed by the GC/MS method was estimated using the number of possible normal alkanes in the sample and the detection limit for normal alkanes. The maximum concentration of normal alkanes was calculated to be 0.15% by weight. The same estimate can not be made for the branched alkanes because of the large unknown number of branched isomers possible in this carbon number range.

The five characteristic resonances for straight carbon chainlength with $C > 10$ are present in the ^{13}C NMR spectrum of 550-700°C saturate fraction (Figure 2). From the integration of these resonances and assuming that the resonances are due to n-alkanes not bonded to any larger molecular moiety, the average carbon chainlength was found to be equal to 14 carbons. An n-alkane of this carbon number has a boiling point of 253°C, which is far too low to be present in this sample. Thus, it is concluded that the observed resonances associated with long, straight carbon chains are due to long, straight carbon chains bonded to a larger molecular moiety. Assuming that the resonance at 14 ppm is equal to one methyl carbon instead of two, the straight carbon chainlength was calculated to be 10 carbons.

Using the ^{13}C DEPT/QUAT spectral data, an average molecule containing 36 carbons with four saturate rings, 11 branch sites, and 11 branches was constructed (Table 5 and Figure 4). There is evidence from the ^{13}C chemical shift data of a small amount of 1,1,2- and 1,1,3-trimethylcyclohexane configuration as with the other two fractions, but these configurations were not illustrated in the average molecular structure. The methyl and methylene carbons were distributed throughout the average molecule representation to give a straight carbon chainlength of 10 carbons to coincide with the observed chemical shift data for a long alkane carbon chain.

>700°C Saturate Hydrocarbon Fraction

The simulated distillation results for this sample (Brown et al. 1986) indicate that 5% by volume distills at a temperature of 506°C. The highest retention time that can be achieved using the GC/MS method corresponds to a normal alkane with a boiling point of 482°C. Thus, the distillate temperature attainable by the GC/MS method (482°C) is significantly below the temperature of the initial boiling material in this sample (506°C). These results indicate that the >700°C saturate hydrocarbon sample is not applicable to analysis using the GC/MS method. However, an attempt using the GC/MS method was made so that the simulated distillation results could be confirmed. The results of this experiment demonstrate that no material in the sample eluted from the gas chromatographic column under the conditions used. Therefore, the GC/MS results are consistent with the simulated distillation results.

The normal ^{13}C NMR spectrum of the $>700^\circ\text{C}$ saturate fraction in Figure 2 shows the characteristic five resonances associated with carbon chainlength greater than 10 carbons. From the integration of these resonances, the carbon chainlength was found to be 15 carbons. The assumption was made that the n-alkanes are not bonded to any other molecular moiety. An n-alkane of 15 carbons has a boiling point of 271°C , which is well below the distillation temperature for this fraction and would not be present. The presence of a long, straight chain alkane as noted from the ^{13}C spectrum must arise from an alkane substituent on a larger molecular moiety. If the methyl resonance at 14 ppm is a result of one methyl carbon, the substituent alkane will have a carbon number of 10 or 11.

The average molecular structure derived from the ^{13}C DEPT/QUAT spectral data is a molecule containing 71 carbons, five saturate rings, 19 branch sites, and 19 branches (Table 5 and Figure 4). The methyl and methylene carbons are distributed so that at least one straight carbon chainlength of 10 carbons is a substituent on a ring.

Distillation Fractions of the Cerro Negro Heavy Petroleum Crude

The original $<200^\circ\text{C}$ distillate fraction of the petroleum crude was further divided into two subfractions, a $<200^\circ\text{C}$ and a $>200^\circ\text{C}$ distillate using a spinning band column distillation procedure. These two fractions were then investigated by NMR and GC/MS spectrometric techniques.

$<200^\circ\text{C}$ Distillate Subfraction

Simulated distillation results are not available for this sample, but the distillation range is estimated to be $98\text{--}216^\circ\text{C}$ based on the GC/MS data.

Evaluation of the GC/MS data detected the presence of four normal alkanes and 15 branched alkanes. The concentration of these compounds in the sample is low. The normal alkanes were identified by comparing the retention times of eluting selected ion peaks in the sample with those of known normal alkanes. The branched alkanes were not as easily identified because of the large number of possible isomers and the closeness and overlapping nature of their retention times in this region of the chromatogram. The branched alkanes were identified only by their carbon number. The alkanes in the $<200^\circ\text{C}$ subfraction are listed in Table 6. The estimated concentration of the individual alkanes was determined using the detection limit data for n-hexadecane (Table 2) and assuming constant sensitivity throughout the carbon number range. The estimated total alkane content for this sample is 2.92% by weight. The total estimated concentration of alkanes is higher than that observed in the saturate hydrocarbon fractions of the Cerro Negro petroleum crude, but it is still not as high as would be expected for a conventional petroleum.

To check the estimated quantities of alkanes present in this sample, it was analyzed using the Western Research Institute's GC/MS hydrocarbon group type analysis. This analytical method was developed

Table 6. Alkanes Detected in the <200°C Distillate Subfraction from the Cerro Negro Heavy Petroleum Crude

Alkane Type	Estimated Concentration in the Sample (Wt %)
Branched C-7	0.07
Branched C-8	0.07
Branched C-8	0.03
n-C8	0.02
Branched C-9	0.21
Branched C-9	0.20
Branched C-9	0.05
Branched C-10	0.10
Branched C-10	0.53
Branched C-10	0.06
Branched C-10	0.11
Branched C-10	0.20
Branched C-10	0.26
n-C10	0.16
n-C11	0.40
Branched C-12	0.06
Branched C-12	0.16
Branched C-12	0.17
n-C12	0.16
Total Alkane Content	2.92

to follow changes in hydrocarbon group type distribution as a function of changes in processing conditions. It has been used successfully in this application (Smith et al. 1986), but the method is not a standardized ASTM method. This method was applied to the analysis of this sample to serve only as a confirmation of the relative magnitude of the alkane concentration.

The results of the GC/MS hydrocarbon group type analysis are provided in Table 7. The concentration of acyclic alkanes determined by this method is 1.2% by weight. The value obtained by this method indicates that the concentration of alkanes in this sample is low and confirms the level of alkanes estimated using the n-hexadecane detection limit data. Other hydrocarbon species detected in this sample include mono- and dicycloalkanes, alkylbenzenes, indanes/tetralins, and naphthalenes.

Table 7. GC/MS Hydrocarbon Group Type Analysis of the <200°C Distillate Subfraction from the Cerro Negro Heavy Petroleum Crude

Z Series	Hydrocarbon Class	Concentration (wt %)
+2	normal and branched alkanes	1.2
0	monocycloalkanes	52.2
-2	dicycloalkanes	40.2
	<u>Total Saturated Hydrocarbons</u>	93.6
-6	alkylbenzenes	3.8
-8	indanes/tetralins	2.4
-12	naphthalenes	0.2
	<u>Total Aromatic Hydrocarbons</u>	6.4

The ^1H and ^{13}C NMR spectra for the <200°C distillate subfraction appear in Figures 5 and 6, respectively. This sample differs from the previously discussed saturate fractions in that the distillate fraction contains both aromatic and aliphatic compounds. The aromatic region in both the ^1H (6.8-7.3 ppm) and the ^{13}C (120-145 ppm) NMR spectra indicates that the aromatic composition is mostly alkylbenzenes with methyl substituents. A small amount of diaromatics and ethyl-substituted benzenes may also be present. The NMR data compliment the GC/MS hydrocarbon group type analysis data (Table 7).

Because of the complexity of the aliphatic region of the ^{13}C NMR spectrum (5-60 ppm), conformational evidence for n-alkanes cannot be made. The carbon and hydrogen type distributions were obtained using the DEPT/QUAT NMR technique. However, reducing these data to average molecular structural parameters is not possible because the distillate fraction is composed of both aromatic and aliphatic hydrocarbons. The carbon and hydrogen type distributions, the atomic H/C ratio, and the hydrogen and carbon aromaticity values calculated from the ^{13}C DEPT/QUAT NMR experiments are listed in Table 8.

>200°C Distillate Subfraction

Simulated distillation results are not available for this sample, but an evaluation of the GC/MS data indicates that the sample has an approximate distillation range of 235-460°C. All normal alkanes within the carbon number range of 13 to 31 were identified in this sample. The concentration of the normal alkanes is only slightly above the detection

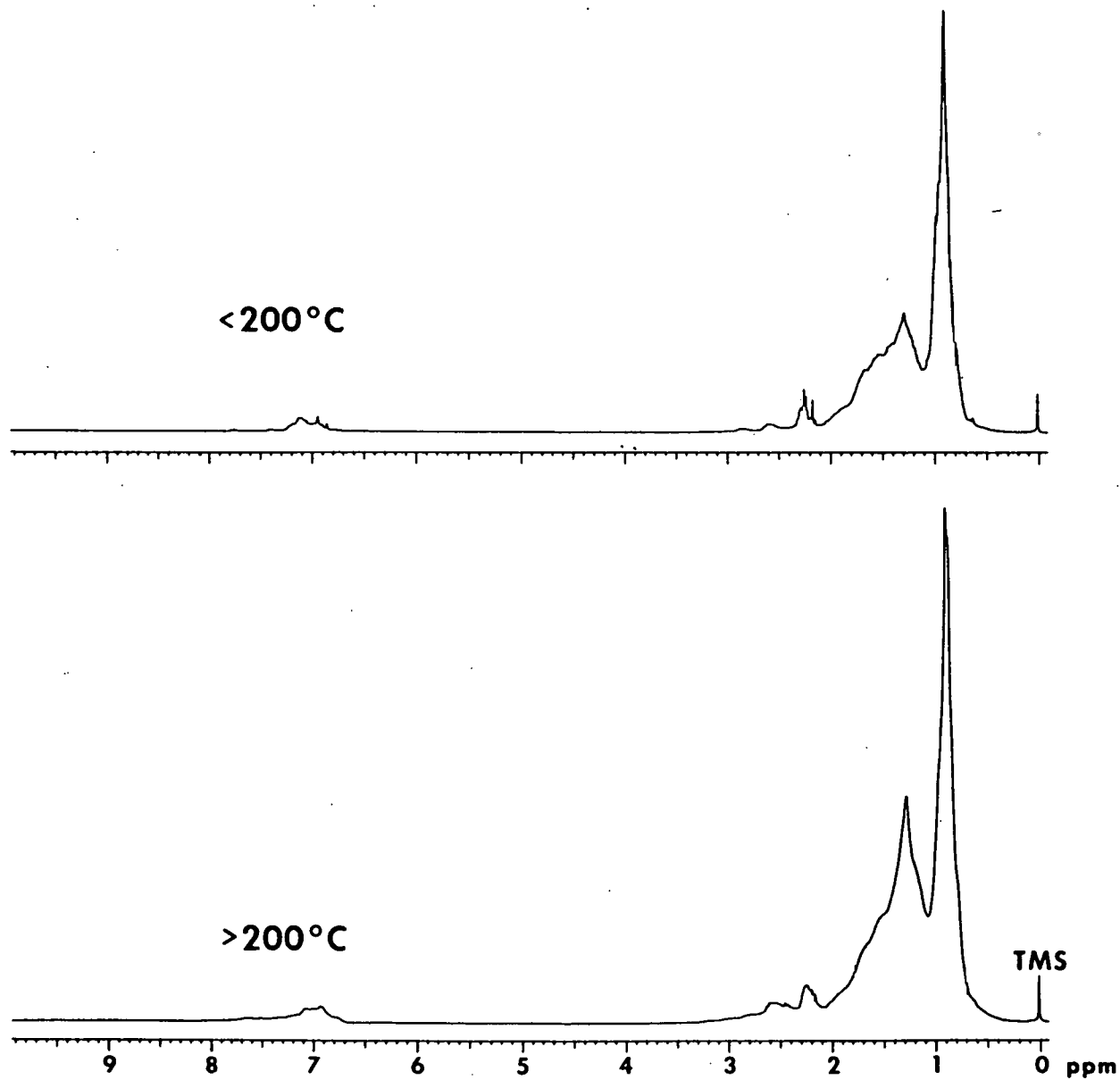


Figure 5. The ^1H NMR Spectra for the <200°C and >200°C Distillate Fractions from the Cerro Negro Heavy Petroleum Crude

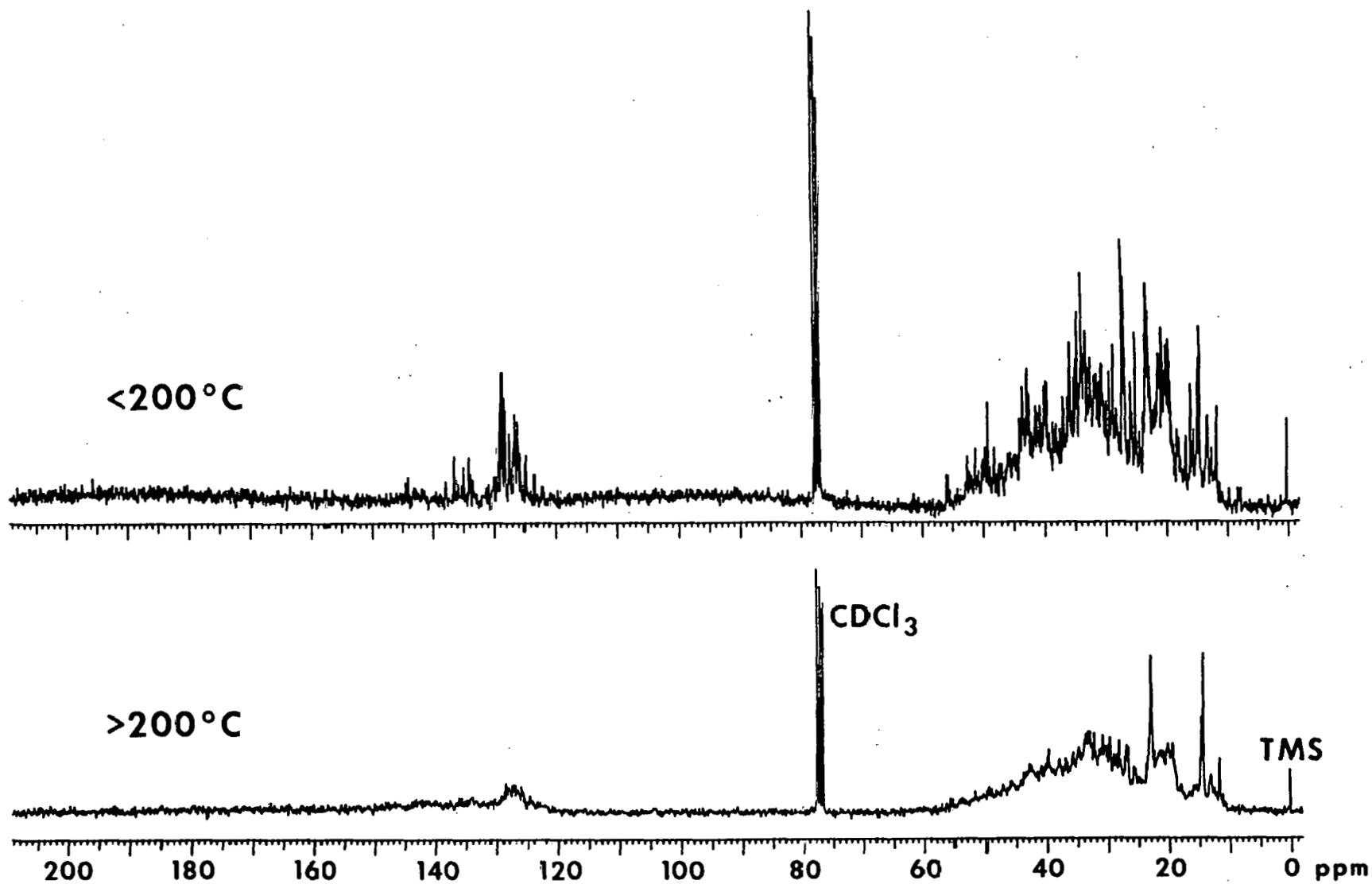


Figure 6. The ^{13}C NMR Spectra for the <math><200^\circ\text{C}</math> and $>200^\circ\text{C}$ Distillate Subfractions from the Cerro Negro Heavy Petroleum Crude

limit of the method. Branched alkanes were not detected. The concentration of the normal alkanes was estimated using the detection limit data for n-hexadecane (Table 2). This was done by assuming a constant sensitivity throughout the carbon number range for the intensity sums for the ions $m/z=57$, 71, 85, and 99. The estimated concentration of the individual normal alkanes in this sample ranged from 0.02% to 0.07% by weight. The total normal alkane concentration was estimated to be 1.05% by weight.

The GC/MS hydrocarbon group type analysis for this sample was not performed because the main objective was to establish the presence of normal and branched alkanes.

Table 8. Carbon and Hydrogen Type Distributions and Structural Parameters for the Distillate Subfractions from the Cerro Negro Heavy Petroleum Crude

Carbon Type	Distillate Subfractions			
	<200°C		>200°C	
	C (atom %)	H (atom %)	C (atom %)	H (atom %)
C				
Aromatic	1.7		5.6	
Aliphatic	6.8		0.0	
CH				
Aromatic	6.2	3.6	6.0	3.2
Aliphatic	34.0	19.9	20.4	10.7
CH ₂	22.7	26.4	39.8	41.9
CH ₃	28.6	50.1	28.1	44.2
Hydrogen Aromaticity (%)		3.6 (2.8) ^a		3.2 (3.5)
Carbon Aromaticity (%)	7.9 (7.5)		11.6 (13.7)	
Atomic H/C	1.71		1.90	

^aValues in parentheses are direct NMR measurements

The ¹H and ¹³C NMR spectra for the >200°C distillate subfraction are also shown in Figures 5 and 6, respectively. A comparison of the spectra indicates similar chemical compositions. However, both

the ^1H and ^{13}C NMR spectra show less resolution than shown in the spectra of the $<200^\circ\text{C}$ distillate oil sample.

The carbon and hydrogen type distributions from ^{13}C DEPT/QUAT NMR spectral data are given in Table 8. The data show that the $>200^\circ\text{C}$ distillate subfraction has a larger proportion of quaternary aromatic carbon due to ring condensation and/or alkyl substitution of the aromatic rings. The increase in the percent of methylene carbon type in the $>200^\circ\text{C}$ distillate subfraction relative to the $<200^\circ\text{C}$ subfraction suggests an increase in number or size of cycloalkanes because the normal ^{13}C spectrum (Figure 6) does not indicate any n-alkanes of C_{10} or greater.

The atomic H/C ratio and the hydrogen and carbon aromaticity values for the $>200^\circ\text{C}$ distillate subfraction are also listed in Table 8. The H/C ratio reflects the increase in methylene carbons and, in general, an increase in the saturate hydrocarbons relative to the $<200^\circ\text{C}$ fraction. There is also an increase in the carbon aromatic content of the $>200^\circ\text{C}$ subfraction relative to the $<200^\circ\text{C}$ subfraction.

CONCLUSIONS

It is concluded from the NMR and GC/MS studies that the Cerro Negro heavy petroleum crude saturate fractions are indeed composed mainly of cycloalkanes with straight carbon chainlength and branched alkane substituents. The ASTM mass spectrometric method D-2786 does not provide an accurate analysis of the normal and branched alkanes but appears to give a reasonably good weight percent distribution of cycloalkanes when compared to NMR average molecular structural parameter calculations.

It is suggested that detailed mathematical and experimental analyses be conducted in an effort to modify the existing ASTM mass spectrometric method D-2786 or that a new method be designed which can be used for non-conventional petroleum crudes such as the Cerro Negro.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement.

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NMR AND GC/MS INVESTIGATION OF THE SATURATE AND DISTILLATE
FRACTIONS FROM THE CERRO NEGRO HEAVY PETROLEUM CRUDE

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