CHARACTERIZATION OF HIGH BOILING FOSSIL
FUEL DISTILLATES VIA ^1H AND ^{13}C NMR ANALYSIS

MASTER

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I. SUMMARY OF TASK OBJECTIVES AND SCOPE FOR THE QUARTER ENDING DECEMBER 31, 1978

The major objective of this quarter was to obtain ^1H NMR spectra for the remaining samples assigned by Department of Energy to date. These included the following:

GACH SARAN Crude Distillates:

- (1) Monoaromatic GPC 206: Fractions 14, 18, 22
- (2) Diaromatic GPC 207: Fractions 15, 21, 24
- (3) Polyaromatic-Polar GPC 208: Fractions 15, 20, 25
- (4) Adsorption Chromatography concentrates: saturates, monoaromatic, polyaromatic-polar (ca. 12 samples)

WILMINGTON Crude Distillates:

- (1) Monoaromatic GPC 209: Fractions 15, 19, 22
- (2) Diaromatic GPC 211: Fractions 16, 19, 24
- (3) Polyaromatic-Polar 210: Fractions 16, 21, 26
- (4) Adsorption Chromatography Concentrates: saturates, monoaromatics, diaromatics, polyaromatic-polar (ca. 12 samples)

Concurrently, it was planned to obtain as many as possible ^{13}C NMR spectra of the monoaromatic fractions requested in the contract. Finally, additional ^{13}C NMR spectra of other fractions would be recorded contingent upon the completion of the above objectives. The usual Ar-C to Al-C ratios and other appropriate calculations were to made also. All new data in the tables are underlined and in italics.

II. ABSTRACT OF PROGRESS TO DATE

The goals reached in the second quarter of the original contract are the completion of the ^1H NMR analysis of all of the concentrates (monoaromatic, diaromatic, polyaromatic-polar and saturates) and GPC (gel permeation chromatography) fractions 211-76 #16 and 24 (diaromatic) and 210-76 #16, 21 and 26 (polyaromatic-polar) distillates (535-670°C) of Wilmington crude and the concentrates and GPC fractions 207-76 #15 and 24 (diaromatic) and 208-76 #15, 20 and 25 (polyaromatic-polar) of Gach Saran crude. In addition, the ^{13}C NMR analysis was completed of the monoaromatic GPC fractions of Wilmington

(209-76 #15 and 23) and Gach Saran (Concentrate and 206-76 #14, 18 and 22) distillates as well as the ^{13}C NMR analysis of the concentrates of the diaromatic, polyaromatic-polar and saturate fractions of Wilmington and Gach Saran distillates. The acquisition of ^{13}C NMR spectra of the remaining fractions is steadily progressing, although long acquisition times (for example, 63 hours per spectrum) will slow somewhat the rate at which data can be obtained.

III. REVIEW OF THE RECENT LITERATURE.

The following review is intended to be a brief outline of the most recent developments in the use of ^1H and ^{13}C NMR spectroscopy in the analysis of fossil fuels (e.g. coals and petroleum). Because of the very rapid and extensive growth in this area of fuel analysis, this review does not attempt to be comprehensive, but instead current examples of the application of ^1H and ^{13}C NMR spectroscopy in this area are given to illustrate the "State of the Art."

It is noteworthy that the first attempts at quantitative analysis of petroleum fractions by NMR spectroscopy occurred over twenty years ago.¹ This pioneering work employed ^1H NMR spectroscopy in conjunction with mass spectroscopy to characterize petroleum fractions using average chemical (elemental) and spectral (integrated areas) parameters. The nomenclature cited in this work is still in use today.

The general analysis was limited in that average carbon containing structures were calculated using parameters measured from the proton spectra. However, the incorporation of data from other analytical techniques (average molecular weight, elemental analysis, infrared spectrometry, etc.) has resulted in several schemes^{2,3,4} to improve the accuracy of the average structural formulas obtained.

Analysis of fossil fuels by ^{13}C NMR spectrometry was significantly slower in developing due to the lower sensitivity and natural abundance of the ^{13}C isotope. The advent of computer techniques as applied to NMR spectroscopy greatly facilitated this development. Early use of accumulated multiple scan methods permitted the successful application of ^{13}C NMR spectroscopy to the analysis of aromatic petroleum fractions over a decade ago.⁵ In addition to the ^{13}C NMR spectral data, ^1H NMR data and elemental analyses of the samples were used in the characterization of the petroleum fractions.

Although the use of accumulated absorption-mode spectra provided the initial impetus for the use of ^{13}C NMR spectrometry as an analytical tool, the method suffered from several problems. The method as applied to the analysis of petroleum fractions^{6,7} used full proton decoupling. No attempt was made to correct the data obtained for possible Nuclear Overhauser Effects (NOE) resulting from this decoupling technique.^{28,29} In addition, the RF power of the observing channel of the spectrometer often reached levels approaching signal saturation, even though stringent precautions were taken.^{5,6,7} The combination of these possible errors, as well as the low quality (by today's standards) of the resulting spectra casts doubt upon the reliability of these early attempts. Nonetheless, this type of analysis, using superconducting magnets to produce high (59 kG) field strengths, provided reasonably reliable data as late as 1976.⁸ However, it was the advent of fast Fourier transform techniques and remarkable advances in solid state computer design which has permitted the acquisition of high quality spectra in reasonably short times and at a much more acceptable unit cost. One of the first applications of the Fourier transform techniques as applied to petroleum analysis was published in 1976 by Shoolery and Budde.⁹ This work included the application of gated-decoupling techniques and the relaxative agent $\text{Cr}(\text{acac})_3$ to

effectively eliminate the NOE and reduce the time of the analyses. The spectra obtained in this way displayed sharp, intense and well resolved signals in the aliphatic carbon region ($\sim 0-40$ ppm from TMS) and broad but well defined bands in the aromatic region ($\sim 100-160$ ppm from TMS). Careful comparisons between the ^{13}C NMR analysis and standard (ASTM) methods revealed small but consistent differences which were attributed to inherent inadequacies in the ASTM method, and thus suggesting that the ^{13}C NMR method provided a significant improvement in fuel analysis. In a later publication,¹⁰ it was suggested that the high level of spectral detail obtained by this method could be utilized as a "fingerprint" of crude oils to aid in the source identification of oil spills.

A recent publication¹¹ has shown that in some crude petroleum samples the concentration of paramagnetic metal ions (e.g. Fe^{3+} , Cu^{2+} and VO_2^{2+}) was sufficiently high that the measured T_1 relaxation times of the carbon types was reduced to less than 0.81s. Consequently, the analyses of the heavy crude oil residues investigated by the authors was done without the aid of a relaxation agent in most cases. However, when refinement of the petroleum samples preceeds the NMR analysis, the use of relaxation agents must still be strongly recommended.

In addition to the analyses of crude petroleum and fractions obtained from petroleum refinement, several analyses of coal derived liquids have appeared in the recent literature.¹²⁻¹⁷ The liquids were derived by one of three basic processes; catalytic hydrogenation^{12,13} followed by refinement in some cases,¹² liquids derived from a solvent refinement process,^{14,15} and liquids derived from reductive alkylation of coal.^{16,17} It was noted in one paper¹² that relative peak intensities of signals in the aliphatic region (0-40 ppm from TMS) of the ^{13}C NMR spectra could be used to predict average alkyl chain lengths when these signals are resolved. Methods^{13,15} of

combining ^1H and ^{13}C NMR data with elemental analyses and average molecular weights via approaches similar to the early ^1H NMR techniques¹ were used to derive average molecular structural parameters. Model compounds have been investigated¹⁴ which were an aid in the assignment of minor signals observed in the ^{13}C NMR spectra for specific types of carbon skeletons. The assignment of specific signals in the ^{13}C NMR spectra of GPC fractions of butylated coal has aided in the qualitative differentiation of successive GPC fractions.¹⁷

Quite recently, several novel NMR techniques have been applied to the area of solid sample fuel analysis.¹⁸⁻²³ These techniques have enabled researchers to obtain spectra¹⁸⁻²² as well as spin-spin and spin-lattice relaxation times²³ of solid samples.

Cross polarization/dipolar decoupling (cross polarization requires special accessories on an NMR unit) techniques have been of significant value to determine the aromaticity of whole (i.e. unrefined) coals,¹⁹ "macerals" (crushed samples) derived from whole coals²⁰ and powdered samples from oil shale.¹⁸ This technique involved irradiation of the proton spectra signals at an RF power of sufficient intensity to eliminate dipole-dipole interactions between the protons and carbons, while simultaneously applying the spin-lock method²¹ to enhance the net carbon magnetization. Magic-angle spinning, which involves physically tipping the sample at an angle of 54.7° with the direction of the applied magic field,²¹ may also be incorporated to further improve the quality of the ^{13}C NMR spectra obtained from solid fuel samples.^{21,22}

Finally, a method has been developed which employs the measured spin-lattice (T_1) and spin-spin (T_2) relaxation times in conjunction with the analysis of electron spin resonance (esr) spectra to rank different coals with respect to carbon content.²³

In summary, it is evident that the area of NMR spectroscopy as applied

to the analysis of fossil fuels is presently undergoing a rapid expansion, due primarily to the current advances in instrumentation and sample handling techniques. Although most of the early investigations were performed on instruments which had undergone considerable modification, the recent availability of commercial spectrometers with these modifications incorporated should provide an increase in the number and quality of output from several groups. Furthermore, the use of stronger magnetic fields ($>47\text{kG}$) will permit higher resolution spectra to be obtained in a shorter time.

Comparison of ^1H and ^{13}C NMR data from several of these studies with the data from our current investigation will be made in the next section of this report.

IV. DETAILED REPORT OF ACCOMPLISHMENTS TO DATE

a. Discussion and Evaluation of Data

The completion of the ^1H NMR analysis of all samples submitted from Department of Energy is the central objective of this report period. In addition, the ^{13}C NMR analysis of the monoaromatic fractions of the Wilmington crude (209-76) and Gach Saran (206-76) distillates ($535\text{--}675^\circ\text{C}$) is discussed herein. The ^{13}C NMR spectra of concentrates of the various GPC fractions have also been completed and are included.

(1) Analysis of Monoaromatic Fraction

The complete ^{13}C NMR analysis of the monoaromatic fractions is reported for the first time below. A brief summary of the results obtained from the ^1H NMR analysis which were given in detail in the last report is included to provide continuity.

Table I lists the data obtained to date from the spectra of the Wilmington monoaromatic fractions. Values presented for the first time are given in italics.

TABLE I
Wilmington Crude (535-675°C) Distillate
GPC 209-76 (Monoaromatic Fractions)

	<u>Concentrate</u>	<u>Mole % of Total H</u>		<u>#22</u>
		<u>#15</u>	<u>#19</u>	
Ar-H	5.3	3.4	5.4	<u>7.4</u>
Al-H	94.7	96.6	94.6	<u>92.6</u>
Ar-H/Al-H	5.3/94.7 (1:17.9)	3.4/96.6 (1:28.4)	5.4/94.6 (1:17.5)	<u>7.4/92.6</u> <u>(1:12.5)</u>
α -H(α -to Ar)	12.4	7.8	13.8	<u>14.5</u>
β -H(β and greater to Ar)	82.3	88.8	80.8	<u>78.1</u>
Term CH_3	28.1	23.6	27.7	<u>33.3</u>
α -H(α to Ar)/ Total Al-H	12.4/94.7 (1:7.6)	7.8/96.6 (1:12.4)	13.8/94.6 (1:6.8)	<u>14.5/92.6</u> <u>(1:6.4)</u>
Term CH_3 / Total Al-H	28.1/94.7 (1:3.4)	23.6/96.6 (1:4.1)	27.7/94.8 (1:3.4)	<u>33.3/92.6</u> <u>(1:2.8)</u>
α -H(α to Ar)/ Term CH_3	12.4/28.1 (1:2.3)	7.8/23.6 (1:3.0)	13.8/27.7 (1:2.0)	<u>14.5/33.3</u> <u>(1:2.3)</u>
Apparent Side Chain Length	>7	>12	>6	<u>>6</u>
Apparent Branches per Chain	0.5	1.0	0.33	<u>0.53</u>
Approx. Diaromatic (mole % of Total H)	2.0	0.3	1.7	<u>3.1</u>
Ar-C/Al-C (mole % of Total C)	27.4/72.6 [†] (1:2.6)	<u>13.2/86.8*</u> <u>(1:6.6)</u>	29.2/70.8 [†] (1:2.4)	<u>22.7/77.3*</u> <u>(1:3.4)</u>
Ar-H/Ar-C	1/5.2 [†]	<u>1/3.9*</u>	1/5.4 [†]	<u>1/3.1*</u>
Al-H/Al-C	1.3/1 [†]	<u>1.1/1*</u>	1.3/1 [†]	<u>1.2/1*</u>
Side Chain Length (from C peak ratios) estimated	C ₁₁ -C ₁₄ [†]	<u>C₁₃-C₁₆*</u>	C ₁₀ -C ₁₂ [†]	<u>C₈-C₁₀*</u>

† Sample contained 0.03 M Cr(acac)₃

* Sample contained 0.05 M Cr(acac)₃

Data for fraction #22 was substituted for data reported for fraction #23 in this report due to insufficient quantity of the latter.

It was shown in the last report that certain trends were evident in this series of fractions. A general increase in the amount of naphthenic material with increasing fraction number was noted. Moreover, the degree of aromaticity of the fractions increased as well. The broadening of the peaks assigned to the terminal methyl (Term CH_3) in successive spectra also strongly suggested a decrease in average side chain length with increasing fraction number. The average branches per chain also seemingly decreased with increasing fraction number, although it was observed that this affect could be artificially produced by an increase in the level of naphthenic material (see page 9, Report I). These same trends were observed in lower boiling fractions (370-535°C) of Wilmington crude^{4c} based on a combination of analytical techniques. It was also reported that the concentrate most closely resembled the center fraction (#19) in each catagory. The substitution of the data from fraction #22 for that of #23 has not altered these conclusions.

The ^{13}C NMR data given in Table I is summarized below:

Concentrate: The aromatic content of the monoaromatic concentrate was calculated from integration of the ^{13}C NMR spectrum as 24.7%. The range of side chain lengths calculated from the relative peak intensities of specifically assigned signals in the ^{13}C NMR spectrum was considerably higher than the minimum length calculated from the proton data. This probably demonstrated the interference of naphthenic signals in the ^1H NMR spectrum in the calculation of the side chain length - an interference which was evident whenever these two values were compared in subsequent analyses. Interestingly, these results can be compared to values obtained from hydrogenated coal liquids which were separated into saturates, monoaromatic, diaromatic and polyaromatic-polar fractions

chromatographed on dual packed columns.¹² The aromaticity of the monoaromatic fraction of hydrogenated Kaiparowits coal was found to be 30% and the average side chain length was found to be ~8 carbons long¹² via ^{13}C NMR analysis.

Fraction #15: The aromaticity of this fraction was found to be 13.8% from the ^{13}C NMR spectrum. This was less than half the value found in the concentrate. The average side chain length was found to be somewhat longer than that in the concentrate, but not of the length to account for the drop in the calculated aromaticity. Hence, it was suggested that the drop in aromaticity was due to a higher level of condensed aromatics in the concentrate as was noted from the approximate level of diaromatic species in Table I. Lower values of aromaticity have been observed in crude oils,⁹ so that the value obtained for fraction #15 did not seem unreasonable.

Fraction #19: The analysis of fraction 19 was noted in the last quarterly report (page 10). Comparison with the other members in the series showed that the aromaticity had increased compared to #15 to a value of 29.2%. The average chain length was found to be less than that of #15, as was to be expected. The rise in aromaticity was easily accounted for since both the ^{13}C and ^1H NMR spectra of this fraction reflected a rise in the level of diaromatic material.

Fraction #22: It was observed that the aromaticity of fraction #22 did not fit the pattern observed in the other fractions. The value of 22.7% for the aromatic carbon content was significantly less than that calculated for fraction #19. It was apparent from the ^{13}C NMR spectrum of fraction #22 that there was a much wider variety of aliphatic side chains as evidenced by the very broad envelope of signals in the aliphatic (0-60 ppm from TMS) portion of the spectrum. Also, it was observed that a higher level of naphthenic material could have contributed to the lowering of the percentage of aromatic material. Because the average side chain length was determined from specific signals (see page 10,

Report I) in the spectrum, they represented only those side chains which fitted the necessary criteria of length and substitution. Hence, the low level of aromaticity observed for fraction #22, coupled with the qualitative observation of broad, intense envelopes in the ^{13}C (and ^1H) NMR spectrum indicated a greater branching with shorter, deverse side chain groups, as well as an increased quantity of naphthenic material. A signal at ~ 19.5 ppm was observed in all of the ^{13}C NMR spectra of the Wilmington monoaromatic fractions. The ratio of peak heights of this signal to that of the terminal CH_3 signal (at δ 14.1 from TMS) ranged from 1.06:1 to 1.39:1 (19.5 ppm peak:14.1 ppm peak) in fractions #15, 19 and 22. The signal was tentatively assigned either to methyl carbons ($-\text{CH}_3$) attached directly to an aromatic ring and ortho to a second alkyl substituent, or to methyl carbons attached to arene rings that were hindered sterically by peri type interactions. The ratio of the peak intensities of the signal at ~ 19.5 ppm to the signal at ~ 14.1 ppm varied from fraction to fraction in a manner that paralleled that observed for the change in Ar-C content (which was variable). Thus these two parameters may possibly be linked by some common structural element. A study of model compounds specifically selected for comparison with signals found in the ^{13}C NMR spectra of coal-tar pitches¹⁶ showed the following results:

$$\delta \text{CH}_3 = 19.1$$

1
~

$$\delta \text{CH}_3 = 19.86$$

2
~

Thus, these type of structures could have been present in the sample, as well as compounds similar to the ones given below:²⁴

Table II contains the data obtained from the ^1H and ^{13}C NMR spectra of the monoaromatic fractions (206-76) of the Gach Saran distillates (535-670°C). As in the case of the Wilmington monoaromatic fractions, the ^1H NMR analysis of these Gach Saran fractions was discussed in detail in Report I and will be only briefly reviewed here. Data presented for the first time is given in italics. A brief appraisal of the data for these fractions follows:

Concentrate: The aromatic carbon content of this fraction as calculated from integrated areas under signals in the ^{13}C NMR spectrum (page 10, Report I) was 23.5%. This was somewhat less than that observed in the monoaromatic concentrate of the Wilmington distillate. (see Table I) but was not unexpected. As was noted in the analysis of the ^1H NMR spectra of these two concentrates outlined in the last report, the Gach Saran fraction displayed a lower level of aromatic protons as well. Although these differences were not large, they closely parallel the findings in the ^{13}C NMR spectra and together they may be considered significant. The side-chain length calculated from the ^{13}C NMR data was $\text{C}_{10}\text{-C}_{12}$. (see page 10, report I, for the method of calculation). Although

TABLE II
Gach Saran (535-675°C) Distillate
GPC 206-76 (Monoaromatic Fractions)

	<u>Concentrate</u>	<u>Mole % of Total H</u>		<u>#22</u>
		<u>#14</u>	<u>#18</u>	
Ar-H	5.0	3.1	4.1	7.2
Al-H	95.0	96.6	95.5	92.8
Ar-H/Al-H	5.0/95.0 (1:19.0)	3.1/96.6 (1:31.2)	4.1/95.5 (1:23.4)	7.2/92.8 (1:12.9)
α -H(α to Ar)	11.2	6.2	12.5	16.2
β -H(β and greater to Ar)	83.8	90.7	83.4	76.6
Term CH_3	23.1	20.3	19.4	23.7
α -H(α to Ar)/ Total Al-H	11.2/95.0 (1:8.5)	6.2/96.6 (1:15.6)	12.5/95.5 (1:7.7)	16.2/92.8 (1:5.7)
Term CH_3 / Total Al-H	23.1/95.0 (1:4.1)	20.3/96.6 (1:4.8)	19.4/95.5 (1:4.9)	23.7/92.8 (1:3.9)
α -H(α to Ar)/ Term CH_3	11.2/23.1 (1:2.1)	6.2/20.3 (1:3.3)	12.5/19.4 (1:1.6)	16.2/23.7 (1:1.5)
Apparent Side Chain Length	>8	>16	>7	>5
Apparent Branches per Chain	0.38	1.2	0.0	0.0
Approx. Diaromatic (mole % of Total H)	1.6	0.0	2.1	3.6
Ar-C/Al-C (mole % of Total C)	<u>23.5/76.5†</u> <u>(1:3.3)</u>	<u>14.2/85.8†</u> <u>(1:6.0)</u>	<u>21.1/78.9†</u> <u>(1:3.7)</u>	<u>20.4/79.6†</u> <u>(1:3.9)</u>
Ar-H/Ar-C	<u>1/4.7†</u>	<u>1/4.6†</u>	<u>1/5.2†</u>	<u>1/2.8†</u>
Al-H/Al-C	<u>1.24/1†</u>	<u>1.13/1†</u>	<u>1.22/1†</u>	<u>1.16/1†</u>
Side Chain Length (from C peak ratios) estimated	<u>C₁₀-C₁₂†</u>	<u>C₁₆-C₂₀†</u>	<u>C₁₃-C₁₅†</u>	<u>C₉-C₁₀†</u>

† Sample contained 0.05 M Cr(acac)₃

this was a somewhat lower range than that observed in the Wilmington fraction, the two ranges overlapped, and the differences were not considered significant.

Fraction #14: The ^{13}C NMR spectrum of this fraction revealed a noticeable increase in the average side-chain length when compared to the concentrate. This confirmed a similar observation made from the ^1H NMR spectra of the concentrate and this fraction in Report I. Interestingly, the average side-chain length predicted from the ^1H NMR data was determined to lay at the lower end of the range predicted by ^{13}C NMR analysis of this fraction. This suggested that the level of naphthenic material in this fraction was less than that found in the concentrate. Indeed, the increase in side-chain length in this case could be more than sufficient to account for the drop in aromaticity.

Fraction 18: As noted in the last report, the ^1H NMR spectral data of this fraction most closely resembled the concentrate than any of the other fractions. This similarity was found in the ^{13}C NMR spectra as seen in Table II. The aromaticity from the ^{13}C NMR data was found to be 21.1%, and the range of side-chain lengths was $\text{C}_{13}\text{-C}_{15}$. The large change in aromaticity paralleled the results found in the analysis of the Wilmington monoaromatic fractions, and thus by this consistency lent support to the accuracy of these observations. However, the accompanying large change in the side-chain lengths for the Gach Saran fractions suggested that higher aromaticity of fraction #18 compared to fraction #14 may in part be due to a decrease in the side-chain length - a decrease not observed between fractions #15 and 19 of the Wilmington fractions.

Fraction #22: A value of 20.4% was determined for the aromaticity of fraction #22 from the ^{13}C NMR spectrum. The average side-chain length was found to range between C_9 and C_{10} . These values conformed with the trends observed in the monoaromatic fractions of the Wilmington distillate, thus supporting the observations made above.

A sharp signal at ~19.5 ppm from TMS was also observed in the ^{13}C NMR spectrum of each of the Gach Saran monoaromatic fractions. However, it was extremely interesting to note the ratio of intensities of this peak to that of the peak assigned to the terminal methyl group at 14.1 ppm (from TMS) was reversed from the ratios observed in the monoaromatic fractions of the Wilmington crude distillates. The ratio calculated for each fraction for both the Gach Saran and Wilmington distillates are listed below:

<u>Wilmington</u>		<u>Gach Saran</u>	
	[19.5]/[14.1]*		[19.5]/[14.1]*
Concentrate	1.30	Concentrate	0.53
#15	1.13	#14	0.59
#19	1.06	#18	0.56
#22	1.39	#22	0.73

*Ratio of peak intensities for peak at 19.5 and 14.1 ppm from TMS.

As stated previously, the signal at ~19.5 ppm could be assigned to methyl carbons attached to an arene ring in a position ortho to another alkyl substituent or to methyl carbons in a sterically hindered peri position.¹⁶ It has been postulated that crude petroleum contains a high level of compounds with structures similar to 1-5.⁹ If the signal did indeed arise from this type of hindered methyl carbon, it may be possible to make quantitative conclusions based upon the ratio of peak intensities of this signal to other selected signals in the spectra. Unfortunately, details of possible relationships must await the acquisition of more ^{13}C NMR data.

The trends observed in both the ^1H and ^{13}C NMR analysis of the monoaromatic fractions of the Gach Saran distillate (535-670°C) were similar to those observed for lower boiling (370-535°C) monoaromatic fractions of Gach Saran distillates via a combination of methods.^{4a} The aromaticities observed for the series of

fractions displayed a range of values from 14.2 to 23.5%. This range was not excessively large when one considered the extensive separatory scheme to which the samples had been subjected. Aromaticity values as low as 7.6%⁹ (for crude Pennsylvania petroleum) and as high as 56%⁵ (for certain African oils) have been observed.

(2) Summary of Analysis of the Monoaromatic Fractions..

As mentioned previously, the aromaticities observed for the monoaromatic concentrates were surprisingly similar to the value observed in the monoaromatic fraction isolated from the chromatographic separation of a coal liquid.¹² The alkyl chain length calculated for this coal liquid fraction was given as C_8 .¹² At present, it must be considered that, although similar chromatographic techniques have been applied, any correlation of NMR data between the monoaromatic fraction obtained from coal liquid and the fraction reported herein, though interesting, could be fortuitous. The low level of aromaticity found in fractions #14 of the Gach Saran distillate and #15 of the Wilmington distillates suggested that these fractions consist mainly of long alkyl chains attached to aromatic cores. This was further supported by the fact that the alkyl region of the ^{13}C NMR spectra showed a very low envelope under the main peaks, which indicated a lack of variety in the types of side chains present. This was seen to contrast with the strong envelope seen in the latter fractions, which indicated a wide variety of shorter side chains¹² and naphthenic material.¹⁴ Trends in the aromaticity coupled with trends in the side chain length suggested that although select signals (see page 10, Report I) corresponding to the side chain carbons were evident in each fraction, the length predicted from these signals did not reflect the overall composition of the latter fractions. It was obvious from the spectra of these fractions (Gach Saran 206-76 #22 and Wilmington 209-76 #22) that the long (C_8 or greater) side chains which gave

rise to these signals (at 14.1, 22.7, 32.7, 29.3 and 29.7 ppm) were not a major part of these fractions. Thus, observations based upon the side-chain lengths derived from relative signal intensities (see page 10, Report I) should be tempered by qualitative observations.

(3) Analysis of Diaromatic Fractions.

The results of the NMR analysis of the diaromatic fractions (211-76 #16, 19, 24 and the concentrate are given in Table III). The addition of the ^1H NMR data for fractions #16 and 24 completes this portion of the analysis. The ^{13}C NMR of fraction #19 and the concentrate were listed in Report I and are given again for continuity. The acquisition of the ^{13}C NMR spectra for fractions #16 and 24 await the availability of sufficient instrument time. A description of the results investigated to date is given below:

Concentrate: The aromaticity of the concentrate was calculated to be 37.1%. This was considerably higher than the aromaticity found for the mono-aromatic concentrate (27.4%). The level of aromatic hydrogens was also found to be higher for the diaromatic concentrate. Again, this value is not excessively high when compared to either the aromaticities of heavy crude oil residues, which range from 22.4 to 38.1%,¹¹ or the aromaticities of FCC charge stocks which ranged from 31% to 38%.⁷

Several signals were evident near 19.5 ppm (from TMS), the two most prominent ones occurred at 19.6 and 19.7 ppm. The occurrence of several peaks in this region could correlate with structures 1 and 2¹⁶ as

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TABLE III.
Wilmington Crude (535-675°C) Distillate
GPC 211-76 (Diaromatic Fractions)

	<u>Concentrate</u>	<u>Mole % of Total H</u>		
		<u>#16</u>	<u>#19</u>	<u>#24</u>
Ar-H	8.6	<u>5.4</u>	8.4	<u>14.0</u>
Al-H	91.4	<u>94.6</u>	91.6	<u>86.0</u>
Ar-H/Al-H	8.6/91.4 (1:10.6)	<u>5.4/94.6</u> (1:17.5)	8.4/91.6 (1:10.9)	<u>14.0/86.0</u> (1:6.1)
α -H(α to Ar)	17.0	<u>9.9</u>	17.8	<u>18.9</u>
β -H(β and greater to Ar)	74.4	<u>80.8</u>	73.8	<u>67.1</u>
Term CH_3	26.8	<u>30.8</u>	24.2	<u>28.1</u>
α -H(α to Ar)/ Total Al-H	17.0/91.4 (1:5.4)	<u>9.9/94.6</u> (1:9.6)	17.8/91.6 (1:5.1)	<u>18.9/86.0</u> (1:4.6)
Term CH_3 / Total Al-H	26.8/91.4 (1:3.4)	<u>30.8/94.6</u> (1:3.1)	24.2/91.6 (1:3.8)	<u>28.1/86.0</u> (1:3.1)
α -H(α to Ar)/ Term CH_3	17.0/26.8 (1:1.6)	<u>9.9/30.8</u> (1:3.1)	17.8/24.2 (1:1.4)	<u>18.9/28.1</u> (1:1.5)
Apparent Side Chain Length	>5	<u>>9</u>	>5	<u>>4</u>
Apparent Branches per Chain	0.0	<u>1.1</u>	-0.10	<u>-0.01</u>
Approx. Diaromatic (mole % of Total H)	5.0	<u>3.2</u>	4.0	<u>9.0</u>
Ar-C/Al-C (mole % of Total C)	37.1/62.9† (1:1.7)	*	39.1/60.9† (1:1.6)	*
Ar-H/Ar-C	1/1/4.3	*	1/4.6	*
Al-H/Al-C	11.5/1	*	1.5/1	*
Side Chain Length (from C peak ratios) estimated	C ₉ -C ₁₁	*	C ₁₀ -C ₁₂	*

† Sample contained 0.05 M Cr(acac)₃

* To be completed

was noted in a previous section. The diaromatic content as indicated by the ^1H NMR spectrum (see Table III) was considerably higher for this concentrate, suggesting that such structures could be present. The side chain lengths ($\text{C}_9\text{-C}_{11}$) were considered to be moderately long.

Fraction #16: As could be seen from Table III, this fraction showed a drop in the amount of aromatic hydrogen analyzed. This was not unexpected; as was noted in Report I, the concentrate was predicted to resemble the center or median fraction (#19), with trends in the values similar to those observed in the previously completed monoaromatic fractions in the series of fractions. The low degree of branching indicated for this fraction in part could be accounted for by an increase in the amount of naphthenic material. This was supported by the value obtained for the $\alpha\text{-H}$ (α to Ar) content (9.9%) which, compared to the levels observed in the monoaromatic fractions, was high.

Fraction #19: The analysis of this fraction was partially described in the last quarterly report. The spectral features of this fraction closely parallel those observed in the concentrate, and most of the deductions made from the concentrate can be applied to this fraction. Notably, four distinct signals centered around 19.6 ppm (from TMS) were observed in the ^{13}C NMR spectrum of this fraction. These signals were indicative of possible polyaromatic and multisubstituted constituents.

Fraction #24: The high aromatic content of this fraction was indicated by the amount of aromatic protons measured in the ^1H NMR spectrum, 14.0%. This was the highest percentage found for any of the samples submitted for analysis to date. A recent study³⁰ correlating percent of aromatic protons in the ^1H NMR spectra with thermal maturation of the aromatic elution fraction of the soluble portion of Australian crude oil gave values of aromatic proton content ranging from 8.5 to 21.9%. The low degree of branching (-0.01) found

in fraction #24, coupled with a very high amount of α -H (α to Ar) (18.9%) strongly suggested that naphthenic material was present to a considerable extent. A heavy degree of diaromatic material was indicated by the extension of the aromatic proton signal pattern beyond δ 7.2 (from TMS) (total band width of δ 8.3 - 6.6).

The data derived from the NMR analysis of the diaromatic fractions (207-76 #15, 21 and 24) of Gach Saran distillates (535⁰⁰ - 675⁰⁰C) is given in Table IV. The ¹³C NMR analysis of these fractions is currently under way. A discussion of the results follows:

Fraction #15: The ¹H NMR of this fraction showed a very sharp signal corresponding to the methylene protons (CH_2) in the side chains. The sharpness of this signal suggested long side chains were present²⁵ in predominance. The low value which was calculated for the average branches per chain (0.3) would seem to indicate a variety of saturated rings and naphthenic material may also be present to some extent.

Completion of the ¹³C NMR analysis of this fraction has been planned in the next quarter.

Fraction #21: A limited discussion of this fraction was presented in Report I for the last quarter. It was observed that this fraction showed an increase in the aromatic proton content compared to fraction #15. The broadness of the methylene (CH_2) signal centered at $\approx$ 1.4 ppm (from TMS) implied an increase in the naphthenic material in comparison to fraction #15. Further evidence of this naphthenic content was found in the extension of the α -H (α to Ar) band downfield beyond δ 3.0.

Fraction #24: The amount of naphthenic material in this fraction was evident from the very broad skirt of the methylene peak centered δ 1.28 (from TMS). The α -H (α to Ar) also extended almost to δ 4.0. A low signal centered

TABLE IV
Gach Saran (535-675°C) Distillate
GPC 207-76 (Diaromatic Fractions)

	Mole % of Total H		
	#15	#21	#24
Ar-H	<u>5.8</u>	9.6	<u>11.9</u>
Al-H	<u>94.2</u>	90.4	<u>88.1</u>
Ar-H/Al-H	<u>5.8/94.2</u> <u>(1:16.2)</u>	9.6/90.4 (1:9.4)	<u>11.9/88.1</u> <u>(1:7.4)</u>
α -H(α to Ar)	<u>10.2</u>	17.2	<u>19.6</u>
β -H(β and greater to Ar)	<u>84.0</u>	73.2	<u>68.5</u>
Term CH_3	<u>20.7</u>	23.9	<u>23.6</u>
α -H(α to Ar)/ Total Al-H	<u>10.2/94.2</u> <u>(1:9.2)</u>	17.2/90.4 (1:5.2)	<u>19.6/88.1</u> <u>(1:4.5)</u>
Term CH_3 / Total Al-H	<u>20.7/94.2</u> <u>(1:4.6)</u>	23.9/90.4 (1:3.8)	<u>23.6/88.1</u> <u>(1:3.7)</u>
α -H(α to Ar)/ Term CH_3	<u>10.2/20.7</u> <u>(1:2.0)</u>	17.2/23.9 (1:1.4)	<u>19.6/23.6</u> <u>(1:1.2)</u>
Apparent Side Chain Length	<u>>9</u>	>5	<u>>4</u>
Apparent Branches per Chain	<u>0.3</u>	-0.1	<u>-0.2</u>
Approx. Diaromatic (mole % of Total H)	<u>3.3</u>	6.1	<u>8.7</u>
Ar-C/Al-C (mole % of Total C)	*	*	*
Ar-H/Ar-C	*	*	*
Al-H/Al-C	*	*	*
Side Chain Length (from C peak ratios) estimated	*	*	*

* To be completed

at δ 8.5 disclosed the possibility that large condensed rings or aromatic heterocyclic compounds could be present. A negative number for the estimation of the apparent side-chain length was also typical of a high naphthenic content. (See Report I, page 16, for an explanation).

(4) Summary of the Analysis of the Diaromatic Fractions.

Trends that were implied by the ^1H NMR analysis of the monoaromatic fractions given in the last quarterly report (page 11, Report I) were observed in the diaromatic fractions. The percent of aromatic protons was shown to increase within a given series of diaromatic fractions. Again, the center fractions of the series (Gach Saran 207-76 #21 and Wilmington 211-76 #19) appeared to be most like the respective concentrates rather than the other fractions in the series. Evidence cited also showed an increase in naphthenic content with increasing fraction number. The limited ^{13}C NMR data recorded to date displays high values for the aromatic carbon. These values are not excessively high when compared to values obtained from ^{13}C NMR spectra of crude petroleum^{6,9} and heavy petroleum residues.¹¹ GPC fractions of asphalt residues from two crude petroleum³ showed proportions of aromatic protons comparable to some of the above diaromatic fractions, though a direct comparison may be questionable due to the different nature of the starting materials. Trends observed in the high boiling (535-670°C) distillate fractions did show strong similarities to those observed in lower boiling distillate fractions.^{4a,b} However, the analysis was based primarily upon mass spectra, with ^1H NMR analysis serving as supporting evidence.

(5) Analysis of the Polyaromatic-Polar Fractions.

Table V outlines the results of the initial NMR analysis of the concentrate and polyaromatic-polar fractions (210-76 #16, 21, and 26) of Wilmington distillates (535-670°C). The ^1H NMR spectra of each fraction has been analyzed.

TABLE V
Wilmington Crude (535-675°C) Distillate
GPC 210-76 (Polyaromatic-Polar Fractions)

	<u>Concentrate</u>	<u>Mole % of Total H</u>		
		<u>#16</u>	<u>#21</u>	<u>#26</u>
Ar-H	<u>5.7</u>	<u>2.5</u>	<u>5.2</u>	<u>9.5</u>
Al-H	<u>94.3</u>	<u>97.5</u>	<u>94.8</u>	<u>90.5</u>
Ar-H/Al-H	<u>5.7/94.3</u> <u>(1:16.5)</u>	<u>2.5/97.5</u> <u>(1:39.0)</u>	<u>5.2/94.8</u> <u>(1:18.2)</u>	<u>9.5/90.5</u> <u>(1:9.6)</u>
α -H(α to Ar)	<u>13.0</u>	<u>7.7</u>	<u>12.2</u>	<u>17.4</u>
β -H(β and greater to Ar)	<u>81.3</u>	<u>89.8</u>	<u>82.7</u>	<u>73.2</u>
Term CH_3	<u>29.9</u>	<u>32.3</u>	<u>27.8</u>	<u>28.3</u>
α -H(α to Ar)/ Total Al-H	<u>13.0/94.3</u> <u>(1:7.2)</u>	<u>7.7/97.5</u> <u>(1:12.7)</u>	<u>12.2/94.8</u> <u>(1:7.8)</u>	<u>17.4/90.5</u> <u>(1:5.2)</u>
Term CH_3 / Total Al-H	<u>29.9/94.3</u> <u>(1:3.2)</u>	<u>32.3/97.5</u> <u>(1:3.0)</u>	<u>27.8/94.8</u> <u>(1:3.4)</u>	<u>28.3/90.5</u> <u>(1:3.2)</u>
α -H(α to Ar)/ Term CH_3	<u>13.0/29.9</u> <u>(1:2.3)</u>	<u>7.7/23.3</u> <u>(1:4.2)</u>	<u>12.2/27.8</u> <u>(1:2.3)</u>	<u>17.4/28.3</u> <u>(1:1.6)</u>
Apparent Side Chain Length	<u>>7</u>	<u>>13</u>	<u>>8</u>	<u>>5</u>
Apparent Branches per Chain	<u>0.53</u>	<u>1.8</u>	<u>0.53</u>	<u>0.1</u>
Approx. Diaromatic (mole % of Total H)	<u>3.3</u>	<u>1.1</u>	<u>3.2</u>	<u>6.9</u>
Ar-C/Al-C (mole % of Total C)	<u>31.4/68.6†</u> <u>(1:2.2)</u>	*	*	*
Ar-H/Ar-C	<u>1/5.5†</u>	*	*	*
Al-H/Al-C	<u>1.4/1†</u>	*	*	*
Side Chain Length (from C peak ratios) estimated	<u>C₉†</u>	*	*	*

* To be completed

† Sampled contained 0.05 M Cr(acac)₃

The ^{13}C NMR spectrum of the concentrate has also been acquired since there was a large quantity of it available. This permitted a high concentration to be used in the analysis, permitting a shorter experimental time to be required. Unfortunately, the amounts available for analysis of the fractions are considerably less. These samples will be examined by ^{13}C NMR analysis as quickly as time permits. A brief discussion of the spectrum of each fraction follows:

Concentrate: The ^1H NMR spectrum of the concentrate displayed a strong signal centered at δ 1.28 (from TMS) corresponding the methylene signal (CH_2). The broad skirt of this signal suggests a wide variety of shorter side chains. The wide band correlating to the protons on carbons α to arenes ($\alpha\text{-H}$) also suggested that the sample contained naphthenic material to a considerable extent. Downfield, it was noted that the aromatic band of proton signals extended well beyond δ 7.2 (from TMS) indicating extensive polyaromatic content, as well as possible heteroaromatic content. In the ^{13}C NMR spectrum of the concentrate, a wide aromatic band (100-150 ppm from TMS) was observed, with two distinct maxima. This strongly implied that condensed ring systems were indeed present. The aromaticity was measured from this band was found to be 31.4%, which was considered high in light of the relatively low aromatic proton content calculated from the ^1H NMR spectrum. This seems highly indicative of the expected high content of polyaromatic, condensed ring systems. The side-chain length calculated from either the ^1H or ^{13}C NMR spectra cannot be considered an accurate representation of the true average (see Report I, page 10, for the method of calculation) side chain length. In the ^{13}C NMR spectrum, the very broad, intense band in the aliphatic region revealed a high content of shorter side-chains which would not contribute to the signals used to calculate the side-chain length.

Fraction #16: Three distinct peaks were observed in the ^1H NMR spectrum

which were attributable to terminal methyl (CH_3) protons. These signals were considered an indication of short, branched alkyl side chains which may have been present in the sample.²⁶ Although the amount of detectable aromatic proton was low (~2.5%) in this fraction, no definitive conclusions can be made concerning the aromaticity of this sample until the ^{13}C NMR spectrum can be examined.

Fraction #21: As has been observed in the other fraction series, this center fraction closely parallels the general characteristic obtained from the spectra of the concentrate. The ^1H NMR spectrum of fraction #21 showed two overlapping terminal methyl (CH_3) signals, which in turn overlapped with the broad skirt of the methylene signal (CH_2) of protons on carbons beta position (and further) from arene rings. A low, broad $\alpha\text{-H}$ ($\alpha\text{-Ar}$) signal, coupled with the broadness of the methylene and methyl signals described above implied that naphthenic material was present. As was observed in the spectrum of the concentrate, the extension of the aromatic proton band beyond δ 7.2 (from TMS) showed that condensed ring aromatic compounds were the major part of the sample.

Fraction #26: This final fraction in the series showed a continuation of the trend of a higher successive content of condensed ring aromatics. Polar heteroaromatics were also likely in this sample, although a more conclusive evaluation of the constitution of the sample must await the results from the ^{13}C NMR analysis.

The proton spectra of the polyaromatic-polar fractions (208-76 #15, 20 and 25) of the Gach Saran distillate (535-670°C) and the proton and carbon spectra of the concentrate have been obtained, and the data from these spectra is detailed in Table VI. A brief description of the results of each spectral analysis is given below:

Concentrate: The most interesting features of the spectra of this sample

TABLE VI
Gach Saran (535-675°C) Distillate
GPC 208-76 (Polyaromatic-Polar Fractions)

	<u>Concentrate</u>	<u>Mole % of Total H</u>		
		<u>#15</u>	<u>#20</u>	<u>#25</u>
Ar-H	<u>7.4</u>	<u>2.9</u>	<u>6.1</u>	<u>12.6</u>
Al-H	<u>92.6</u>	<u>97.1</u>	<u>93.9</u>	<u>87.4</u>
Ar-H/Al-H	<u>7.4/92.6</u> <u>(1:12.5)</u>	<u>2.9/97.1</u> <u>(1:33.2)</u>	<u>6.1/93.9</u> <u>(1:15.4)</u>	<u>12.6/87.4</u> <u>(1:6.9)</u>
α -H(α to Ar)	<u>14.8</u>	<u>9.4</u>	<u>14.8</u>	<u>19.8</u>
β -H(β and greater to Ar)	<u>77.8</u>	<u>87.6</u>	<u>79.0</u>	<u>67.6</u>
Term CH_3	<u>22.5</u>	<u>20.5</u>	<u>23.2</u>	<u>23.0</u>
α -H(α to Ar)/ Total Al-H	<u>14.8/92.6</u> <u>(1:6.2)</u>	<u>9.4/97.1</u> <u>(1:10.3)</u>	<u>14.8/93.9</u> <u>(1:6.3)</u>	<u>19.8/87.4</u> <u>(1:4.4)</u>
Term CH_3 / Total Al-H	<u>22.5/92.6</u> <u>(1:4.1)</u>	<u>20.5/97.1</u> <u>(1:4.7)</u>	<u>23.2/93.9</u> <u>(1:4.0)</u>	<u>23.0/87.4</u> <u>(1:3.8)</u>
α -H(α to Ar)/ Term CH_3	<u>14.8/22.5</u> <u>(1:1.5)</u>	<u>9.4/20.5</u> <u>(1:2.2)</u>	<u>14.8/23.2</u> <u>(1:1.6)</u>	<u>19.8/23.0</u> <u>(1:1.2)</u>
Apparent Side Chain Length	<u>>6</u>	<u>>10</u>	<u>>6</u>	<u>>4</u>
Apparent Branches per Chain	<u>0.0</u>	<u>0.4</u>	<u>0.04</u>	<u>-0.22</u>
Approx. Diaromatic (mole % of Total H)	<u>5.1</u>	<u>1.6</u>	<u>4.2</u>	<u>9.2</u>
Ar-C/Al-C (mole % of Total C)	<u>31.0/69.0†</u> <u>(1:2.2)</u>	*	*	*
Ar-H/Ar-C	<u>1/4.2†</u>	*	*	*
Al-H/Al-C	<u>1.34/1†</u>	*	*	*
Side Chain Length (from C peak ratios) estimated	<u>C₁₀-C₁₄†</u>	*	*	*

† Sampled contained 0.05 M Cr(acac)₃

* To be completed

was that they in no way resembled the spectra obtained from the polyaromatic-polar concentrate obtained from the Wilmington distillate. In the ^1H NMR spectra of Gach Saran concentrate the sharp signal arising from the methylene signals of the side chains was much narrower than the corresponding signal in the spectrum of the Wilmington concentrate. The terminal methyl signal in the proton spectrum of this concentrate was less intense than the terminal methyl signal in the Wilmington sample. In the ^{13}C NMR spectra, the aliphatic region (0-50 ppm from TMS) did not show the strong, broad envelope of signals evident in the Wilmington concentrate. Instead, sharp signals attributable to long side-chains dominated this region. Thus, the range of 10-14 carbons per side chain could be considered as a fair estimate. Interestingly, the aromaticity (from the ^{13}C NMR spectrum) of the Gach Saran concentrate (31.0%) did not differ significantly from that observed in the Wilmington concentrate (31.4%). On the other hand, the percent of aromatic protons did show a noticeable difference (7.4% in the Gach Saran concentrate compared to 5.7% in the Wilmington sample). This could be attributed to a lower degree of substitution on an assumed benzene-type nucleus in the Gach Saran sample.

Fraction #15: The ^1H NMR spectrum of this sample showed a decrease in the aromatic proton fraction compared to the concentrate. A drop in the $\alpha\text{-H}$ (α to Ar) and terminal methyl (term CH_3) content implied that longer alkyl chains were present when compared to the concentrate. A reduction in the number of rings per average condensed ring aromatic structure was inferred from the drop in the integral intensity for proton-signal beyond δ 7.2 (from TMS).

Fraction #20: The proton spectrum of this fraction and the data derived from it so closely resembles that of the concentrate that the deductions made from the ^1H NMR spectrum of the concentrate were applicable to this fraction

as well. Of course this was not unexpected, since this further confirmed the observation of trends in the aromaticity, side-chain length and naphthenic content in all of the other series considered to date.

Fraction #25: The methylene and terminal methyl signals in the proton spectrum of this fraction displayed a broadness near the baseline, suggesting a variety of side chain lengths as well as naphthenic ring compounds were present to a greater degree than fraction #20. A large increase in the percent of aromatic protons (compared to #20) may have arisen from an increase in the average number of aromatic rings per molecule. The negative value (-0.22) (see Report I, page 16, for the method of calculation) calculated for the average branches per chain and the broad α -H (α to Ar) signal between δ 2.1 - 4.0 (from TMS) gave an indication of the large naphthenic content.

(6) Summary of the Polyaromatic-Polar Analysis.

Strong trends were observed in each of the above series of fractions. Both series showed a steady increase in aromatic proton fractions, diaromatic proton content and α -H (α to Ar) levels. The side chain length showed a steady decrease with increasing fraction number, indicating both a decrease in side chain length and an increase in naphthenic material. In contrast, the two series were seen to be very different from one other both in quantitative (e.g. aromatic carbon and proton content) and qualitative (e.g. proton signal widths) aspects. The portent of this observation will be further explored in the soon to be acquired ^{13}C NMR spectra.

(7) Analysis of the Saturate Fractions.

The saturate fractions of the Gach Saran and Wilmington distillates have been investigated by both ^1H and ^{13}C NMR techniques and are summarized in Table VII and outlined below:

Wilmington Saturate: The proton spectrum displayed a very low (0.9%)

TABLE VII
Saturate Fractions of Gach Saran ("A" 9-29-76) and
Willmington ("H" 9-29-76) Distillates (535-675°C)

	Mole % of Total H	
	GS "A"	W1 "H"
Ar-H	<u>0.9</u>	<u>0.9</u>
Al-H	<u>99.1</u>	<u>99.1</u>
Ar-H/Al-H	<u>0.9/99.1</u> <u>(1:106)</u>	<u>0.9/99.1</u> <u>(1:105)</u>
α -H(α to Ar)	<u>2.5</u>	<u>2.6</u>
β -H(β and greater to Ar)	<u>96.5</u>	<u>96.4</u>
Term CH_3	<u>26.0</u>	<u>33.6</u>
α -H(α to Ar)/ Total Al-H	<u>2.5/99.1</u> <u>(1:38.8)</u>	<u>2.6/99.1</u> <u>(1:37.5)</u>
Term CH_3 / Total Al-H	<u>26.0/99.1</u> <u>(1:3.8)</u>	<u>33.6/99.1</u> <u>(1:2.9)</u>
α -H(α to Ar)/ Term CH_3	<u>2.5/26.0</u> <u>(1:10.2)</u>	<u>2.6/33.6</u> <u>(1:12.9)</u>
Apparent Side Chain Length	<u>39.0</u>	<u>37.0</u>
Apparent Branches per Chain	<u>6.0</u>	<u>7.5</u>
Approx. Diaromatic (mole % of Total H)	<u>0.0</u>	<u>0.0</u>
Ar-C/Al-C (mole % of Total C)	<u>7.6/92.4*</u> <u>(1:12.2)</u>	<u>5.9/94.1*</u> <u>(1:16.0)</u>
Ar-H/Ar-C	<u>1/8.4*</u>	<u>1/6.6*</u>
Al-H/Al-C	<u>1.07/1*</u>	<u>1.05/1*</u>
Side Chain Length (from C peak ratios) estimated	<u>C₂₁-C₂₇*†</u>	<u>C₁₉-C₂₈*†</u>

* Sample contained 0.05 M. Cr(acac)₃

† Calculated for paraffinic carbon chains

aromatic content, as would be expected for a saturate fraction. The carbon spectrum also indicated a low but detectable aromaticity (7.6%). This suggested that the usual methods for calculating side chain lengths from the α -H (α to Ar): Total Al-H ratio would prove invalid, since much of the alkyl content could be attributed to parafinic material. A calculation of the alkyl chain length was made using peak ratios from the carbon spectrum using an alternate equation. The assumption was made that all alkyl signals present in the carbon spectrum were due to parafinic material not attached to arene rings. Branching and naphthenic material were assumed to contribute little to the peaks used in the analysis. Thus, the intensity of signals corresponding to the terminal methyl carbon, and the carbons one, two and three atoms removed from the terminus were compared to the strong signal due to the carbons five or more carbons away from a terminus (see below):

The relationship used was:

$$n = 2[5] / X$$

where:

n = The number of carbon atoms 5 or greater from the terminus.

$[5]$ = The intensity of the signal corresponding to carbons 5 or greater from the terminus.

$[X]$ = The intensity of one of the sets of carbon signals (1,1';2,2', etc.).

The factor of two arose from the fact that signals for carbons 1 and 1' were expected to overlap. Calculation of the total length followed by simply adding $(n + 8)$ to account for the 1, 1', 2, 2', 3, 3', 4 and 4' carbons. The results of these calculations are given in Table VII for both the Wilmington and Gach Saran fractions.

The proton spectrum of the Wilmington fraction qualitatively showed a broadness near the baseline of the methylene signal ($\sim\delta$ 1.28) which suggested a considerable amount of saturate ring compounds could have been present. It was also considered likely that what little aromatic material was present was in the form of naphthenic material. A signal at 19.7 ppm (from TMS) was attributed to structures of the type below:

Gach Saran Saturate: The Gach Saran fraction differed from the Wilmington fraction in that it showed a lower level of terminal methyl (CH_3) protons (26.0% compared to 33.6%). The signals also were much narrower than those observed in the ^1H NMR spectrum of the Wilmington fraction. However, in all other categories, the two saturate fractions resembled each other very closely.

(8) Summary of the Analysis of the Saturate Fractions.

In the ^{13}C NMR spectrum of each of the fractions a signal at 19.7 ppm was attributed to methyl groups ortho to another alkyl group on an arene ring. This conclusion was based upon an analogy with an evaluation of a study of the ^{13}C NMR spectra of coal extracts in the literature¹⁴ and model compound data.²⁴ However, it should be noted that this same signal could be attributed to branching methyl groups in certain environments. Shifts in this region have been calculated and observed for methyl groups attached to polymeric carbon chains.²⁷ At present, the overall importance of this signal cannot therefore be assessed.

A compilation of all data presented in this report is given in Table VIII. Those values listed in italics are provided for the first time in this report.

For convenience, we have developed Figure 1 to show the variation profile in $\text{Ar-C}/\text{Al-C}$ from various fractions of Gach Saran and Wilmington high boiling distillates.

TABLE VIII Summary of Data to Date

Source	Ar-H ^a	Al-H ^a	Ar-H Al-H	α -H ^{a,b}	β -H ^{a,c}	Term. CH ₃ ^d	α -H ^b Tot. Al-H	Term. CH ₃ Tot. Al-H	α -H ^b Term. CH ₃	Appar. side ch. len.	Appar. br./ch.	Approx. Diar.	Ar-C ^{d,f} Al-C	Ar-H ^{e,f} Ar-C	Al-H ^{e,f} Al-C
Wilmington Crude															
Monoaromatic															
Concentrate	5.3	94.7	1/17.9	12.4	82.3	28.1	1/7.6	1/3.4	1/2.3	7	0.5	2.0	1/2.6	1/5.2	1.3/1
GPC 209-76 #15	3.4	96.6	1/28.4	7.8	88.8	23.6	1/12.4	1/4.1	1/3.0	12	1.0	0.3	1/6.6	1/3.9	1.1/1
GPC 209-76 #19	5.4	94.6	1/17.5	13.8	80.8	27.7	1/6.8	1/3.4	1/2.0	6	0.33	1.7	1/2.4	1/5.4	1.3/1
GPC 209-76 #23	8.3	91.7	1/11.0	15.9	75.8	30.7	1/5.8	1/3.0	1/1.9	5	0.29	4.1	1/3.4	1/3.1	1.2/1
Diaromatic															
Concentrate	8.6	91.4	1/10.6	17.0	74.4	26.8	1/5.4	1/3.4	1/1.6	5	0.00	5.0	1/1.7	1/4.3	1.5/1
GPC 211-76 #16	5.4	94.0	1/17.5	9.9	80.8	30.8	1/9.8	1/3.1	1/3.1	9	1.10	3.2			
GPC 211-76 #19	8.4	91.6	1/10.9	17.8	73.8	24.2	1/5.1	1/3.8	1/1.4	5	-0.10	4.0	1/1.6	1/4.6	1.5/1
GPC 211-76 #24	14.0	88.0	1/6.1	18.9	67.1	28.1	1/4.6	1/3.1	1/1.5	4	-0.01	9.0			
Polyaromatic-Polar															
Concentrate	5.7	94.3	1/16.5	13.0	81.3	29.9	1/7.2	1/3.2	1/2.3	7	0.53	3.3	1/2.5	1/5.0	1.3/1
GPC 210-76 #16	2.5	97.6	1/39.0	7.7	89.8	32.3	1/12.7	1/3.0	1/4.2	13	1.8				
GPC 210-76 #21	5.2	94.8	1/18.2	12.2	82.7	27.8	1/7.8	1/3.4	1/2.3	8	0.53				
GPC 210-76 #26	9.5	90.6	1/9.6	17.4	73.2	28.3	1/5.2	1/3.2	1/1.6	5	0.1				
Saturate Fraction	0.9	99.1	1/105	2.6	98.4	33.8	1/37.5	1/2.9	1/12.7	37	0.0	0.0	1/16.0	1/6.6	1.05/1
Cach Saran Crude															
Monoaromatic															
Concentrate	5.0	95.0	1/19.0	11.2	83.8	23.1	1/8.5	1/4.1	1/2.1	8	0.4	1.6	1/3.3	1/4.7	1.24/1
GPC 206-76 #14	3.1	96.9	1/31.2	6.2	90.7	20.3	1/15.6	1/4.8	1/3.3	15	1.2	0.0	1/6.0	1/4.6	1.13/1
GPC 206-76 #18	4.1	95.9	1/23.4	12.5	83.4	19.4	1/7.7	1/4.9	1/1.6	7	0.0	2.1	1/3.7	1/5.2	1.22/1
GPC 206-76 #22	7.2	92.8	1/12.9	16.2	76.6	23.7	1/5.7	1/3.9	1/1.5	5	0.0	3.6	1/3.9	1/2.8	1.18/1
Diaromatic															
GPC 207-76 #15	5.8	94.2	1/16.2	10.2	84.0	20.7	1/9.2	1/4.8	1/2.0	9	0.3	3.3			
GPC 207-76 #21	9.6	90.4	1/9.4	17.2	73.2	23.9	1/5.2	1/3.8	1/1.4	5	-0.1	6.1			
GPC 207-76 #24	11.9	88.1	1/7.4	19.6	68.5	23.8	1/4.5	1/3.7	1/1.2	4	-0.2	8.7			

TABLE VIII (Continued)

Source	Ar-H ^a	Al-H ^a	$\frac{\text{Ar-H}}{\text{Al-H}}$	$\alpha\text{-H}^{a,b}$	$\beta\text{-H}^{a,c}$	Term. CH ₃ ^d	$\alpha\text{-H}^b$ Tot. Al-H	Term. CH ₃ ^d	$\alpha\text{-H}^b$ Term. CH ₃	Appar. side ch. len.	Appar. br./ch.	Approx. Diar.	$\frac{\text{Ar-C}^d}{\text{Al-C}}$	$\frac{\text{Ar-H}^e}{\text{Ar-C}}$	$\frac{\text{Al-H}^e}{\text{Al-C}}$
<i>Gach Saran Crude</i>															
<i>Polyisomatio-Polar</i>															
<i>Concentrate</i>	7.4	92.8	1/12.5	14.8	77.8	22.5	1/6.2	1/4.1	1/1.5	8	0.0	5.1	1/2.2	1/4.2	1.34/1
GPC 208-76 #15	2.9	97.1	1/33.2	9.4	87.8	20.5	1/10.3	1/4.7	1/2.2	10	0.4				
GPC 208-76 #20	6.1	93.9	1/15.4	14.8	79.0	23.2	1/6.3	1/4.0	1/1.6	8	0.04				
GPC 208-76 #25	12.8	87.4	1/6.9	19.8	67.8	23.0	1/4.4	1/3.8	1/1.2	4	-0.22				
<i>Saturate Fraction</i>	0.9	99.1	1/106	2.5	96.5	28.0	1/38.8	1/3.8	1/10.2	39	0.0	0.0	1/12.2	1/8.4	1.07/1
<i>Sat. Frac. Fr. Oil</i>															
#1465	0.6	99.4	1/166	3.3	96.1	27.3	1/30	1/3.6							
#1480	0.5	99.5	1/199	2.1	97.4	27.8	1/47.4	1/3.6							
#1498	0.6	99.4	1/166	0.8	98.6	33.1	1/165	1/3.0							
#1570	0.5	99.5	1/199	1.9	97.6	28.8	1/52.4	1/3.4							
#1553	0.6	99.4	1/166	0.6	98.8	33.1	1/165	1/3.0					1/18.6	1/10.2	1.05/1
#1553-HPLC	0.0	100.0	0.0	0.0	100.0	32.2	0.0	1/3.1					1/24.6	1/7.8	1.03/1
#39-1484	0.0	100.0	0.0	0.0	100.0	30.4	0.0	1/3.3					0.0	0.0	1.0
S11-A1 #355	0.0	100.0	0.0	0.0	100.0	30.5	0.0	1/3.3					0.0	0.0	1.0

^a Mole % of total proton integral. ^b Protons on carbons α to arenes. ^c Protons on carbons β or greater to arenes.
^d Expressed in mole % of total carbon integral. ^e Ratio of mole % of the total proton integral vs mole % of total carbon integral. ^f All carbon spectra were recorded using gated decoupling techniques. Cr(acac)₃ was used as a relaxation agent when sample size dictated it.

Figure 1. Aromatic carbon (○) and proton (□) content of the monoaromatic GPC fractions of Wilmington (209-76, left) and Gach Saran (206-76, right) distillates expressed as per cent of the total carbon or proton integrated areas of the respective NMR spectra.

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^{13}C NMR Spectrum of Oil, Wilmington MA GPC 209-76 #15 (see Table I)

PFT X CW ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 110,000
 Size. . 8K; P2/RF. . 8.8 μs /dB; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . ^2H ; D5/ST. . . 0.7 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

¹H NMR Spectrum of Oil, Wilmington MA GPC 209-76 #22 (see Table I)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85776 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.6
 Size. . NA K; P2/RF. . . 63 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

^{13}C NMR Spectrum of Oil, Wilmington MA GPC 209-76 #22 (see Table I)

PFT X CW ; Solvent. . . DCCl_3 ; SO. . 35101 Hz ; PW. . 5000 Hz ; T. . . 37°C ; Acq/SA. . 27,900
 Size. . 8 K ; P2/RF. . 8.8 $\mu\text{s/dB}$; SF. . 25.2 MHz ; FB. . ± 3 KHz ; Lock. . ^2H ; D5/ST. . . 0.7 s
 DC. . ^1H ; Gated Off. . Delay ; Offset. . 45308 Hz ; RF. . 9 W/dB ; NBW. . Sq Wv 100 Hz

¹H NMR Spectrum of Oil, Wilmington DA GPC 211-76 #16 (see Table III)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 83701 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.25
Size. . NA K; P2/RF. . . 65 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . ¹H; D5/ST. . . 250 s
DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Wilmington DA GPC 211-76 #24 (see Table II)

PFT _ CW X ; Solvent. . . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.6
Size. .NA K; P2/RF. . . 61 μs/dB; SF. . 100.1 MHz; FB. . . . 2 Hz; Lock. . ²H; D5/ST. . 250 s
DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Wilmington PAP Concentrate 10-4-76 (see Table V)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
 Size. . NA K; P2/RF. . . 52 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

^{13}C NMR Spectrum of Oil, Wilmington PAP Concentrate 10-4-76 (see Table V)

PFT X CW _ ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 7000
 Size. . 8 K; P2/RF. . 10.0 μs /dB; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . . ^2H ; D5/ST. . 7.0 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

¹H NMR Spectrum of Oil, Wilmington PAP GPC 210-76 #16 (see Table V)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.25
 Size. . NA K; P2/RF. . . 65 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA; Gated Off. . . NA; Offset. . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Wilmington PAP GPC 210-76 #21 (see Table V)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
 Size. . NA K; P2/RF. . 66 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . NA Hz

¹H NMR Spectrum of Oil, Wilmington PAP GPC 210-76 #26 (see Table V)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 2.0
 Size. . NA K; P2/RF. . . 70 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . ²H; D5/ST. . . 250 s
 DC. . NA ; Gated Off. . NA ; Offset. . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Wilmington Saturate 9-29-76 (see Table VII)

PFT _ CW X ; Solvent. . . . DCCl₃; SO. . 85772 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
Size. .NA K; P2/RF. . . 57 μ s/dB; SF. . 100.1 KHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
DC. . NA ; Gated Off. . . NA ; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

^{13}C NMR Spectrum of Oil, Wilmington Saturate 9-29-76 (see Table VII)

PFT X CW ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 6,600
 Size. . 8K; P2/RF. . 10.0 $\mu\text{s/dB}$; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . . ^2H ; D5/ST. . . 7.0 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . 3q Wv 100 Hz

¹³C NMR Spectrum of Oil, Gach Saran MA Concentrate 9-26-76 (see Table II)

PFT X CW _ ; Solvent. . . DCCl₃; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 110,000
 Size. . 8K; P2/RF. . 8.8 μs/dB; SF. . 25.2 MHz; FB. . ±3 KHz; Lock. . . ²H; D5/ST. . . 0.7 s
 DC. . ¹H; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

^{13}C NMR Spectrum of Oil, Gach Saran MA GPC 206-76 #14 (see Table II)

PFT X CW _ ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 193,000
 Size. . 8K; P2/RF. . 8.8 μs /dB; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . ^2H ; D5/ST. . . 0.7 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . 5q Wv 100 Hz

^{13}C NMR Spectrum of Oil, Gach Saran MA GPC 206-76 #18 (see Table II)

PFT X CW ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 109,000
 Size. . 8K; P2/RF. . 8.8 μs /dB; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . ^2H ; D5/ST. . . 0.7 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

^{13}C NMR Spectrum of Oil, Gach Saran MA GPC 206-76 #22 (see Table II)

PFT X CW ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . 37°C; Acq/SA. . 126,000
 Size. . 8K; P2/RF. . 8.8 $\mu\text{s}/\text{dB}$; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . ^2H ; D5/ST. . . 0.7 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

¹H NMR Spectrum of Oil, Gach Saran DA GPC 207-76 #15 (see Table IV)

PFT _ CW X ; Solvent. . . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . . 1.0
Size. .NA K; P2/RF. . . 61 μ s/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . , ²H; D5/ST. . . 250 s
DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

^1H NMR Spectrum of Oil, Gach Saran DA GPC 207-76 #24 (see Table IV)

PFT _ CW X ; Solvent. . DCCl_3 ; SO. . 85771 Hz; PW. . 1000 Hz; T. . 37 °C; Acq/SA. . 1.0
 Size. . NA K; P2/RF. . . 72 $\mu\text{s/dB}$; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . ^2H ; D5/ST. . 250 s
 DC. . NA; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Gach Saran PAP Concentrate 10-4-76 (see Table VI)

PFT _ CW X ; Solvent. . . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
 Size. . 8K; P2/RF. . . 50 μs/dB; SF. . 100.1 MHz; FB. . . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA ; Gated Off. . NA ; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

^{13}C NMR Spectrum of Oil, Gach Saran PAP Concentrate 10-4-76 (see Table VI)

PFT X CW ; Solvent. . . DCCl_3 ; SO. . 35101 Hz; PW. . 5000 Hz; T. . . 37 °C; Acq/SA. . 27,000
 Size. . 8K; P2/RF. . 8.8 $\mu\text{s/dB}$; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . ^2H ; D5/ST. . . 0.7 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

¹H NMR Spectrum of Oil, Gach Saran PAP GPC 208-76 #15 (see Table VI)

PFT _ CW X ; Solvent. . . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.6
 Size. .NA K; P2/RF. . . 63 μs/dB; SF. .100.1 MHz; FB. . . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA ; Gated Off. . . NA ; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Gach Saran PAP GPC 208-76 #20 (see Table VI)

PFT _ CW X ; Solvent. . . . DCCl₃; SO. . 85775 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
 Size. . 8K; P2/RF. . . -61 μs/dB; SF. . 100.1 MHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA ; Gated Off. . NA ; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Gach Saran PAP GPC 208-76 #25 (see Table VI)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
 Size. .NA K; P2/RF. . . 61 μs/dB; SF. .100.1 MHz; FB. . . 2 Hz; Lock. . ²H ; D5/ST. . 250 s
 DC. . NA ; Gated Off. . . NA ; Offset. . . NA Hz; RF. .NA W/dB; NBW. . . . NA Hz

¹H NMR Spectrum of Oil, Gach Saran Saturate 9-29-76 (see Table VII)

PFT _ CW X ; Solvent. . . DCCl₃; SO. . 85771 Hz; PW. . 1000 Hz; T. . . 37 °C; Acq/SA. . 1.0
 Size. . NA K; P2/RF. . 40 μs/dB; SF. . 100.1 KHz; FB. . . 2 Hz; Lock. . . ²H; D5/ST. . 250 s
 DC. . NA ; Gated Off. . . NA; Offset. . . NA Hz; RF. . NA W/dB; NBW. . . . NA Hz

^{13}C NMR Spectrum of Oil, Gach Saran Saturate 9-29-76 (see Table VII)

PFT X CW _ ; Solvent. . . DCCl_3 ; SO. . 35701 Hz; PW. . 5000 Hz; T. . . 37°C; Acq/SA. . 21,740
 Size. . 8K; P2/RF. . 10.0 μs /dB; SF. . 25.2 MHz; FB. . ± 3 KHz; Lock. . ^2H ; D5/ST. . . 1.2 s
 DC. . ^1H ; Gated Off. . Delay; Offset. . 45308 Hz; RF. . 9 W/dB; NBW. . Sq Wv 100 Hz

IV. WORK PLANNED FOR NEXT QUARTER

The thrust for the remainder of the contract will be to acquire the ^{13}C NMR spectra which have not been recorded to date. The proposed order will be first to obtain spectra for the diaromatic fractions and then the polyaromatic-polar fractions. The order will, of course, be subject to changes depending upon the sample characteristics and any suggestions from Department of Energy. Due to the limited amount of most of the remaining samples, a minimum of 63 hours per spectrum may be required. Careful monitoring of the experiment will be necessary to minimize data acquisition times which could result in the loss of the purified sample due to the contamination by the added relaxation agent.

VI. ACKNOWLEDGMENTS

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