

Qualitative and Quantitative Analysis of Heavy Crude Oil Samples and Their SARA Fractions with ¹³C Nuclear Magnetic Resonance

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Keywords: aromaticity, SARA, quantitative composition, oil fraction, crude oil, ¹³C NMR spectroscopy

Abstract:

Nuclear magnetic resonance (NMR) approaches have unique advantages in the analysis of crude oil because they are non-destructive and provide information on chemical functional groups. Nevertheless, the correctness and effectiveness of NMR techniques for determining saturates, aromatics, resins, and asphaltenes (SARA analysis) without oil fractioning are still not clear. In this work we compared the measurements and analysis of high-resolution ¹³C NMR spectra in B₀ = 16.5 T (NMR frequency of 175 MHz) with the results of SARA fractioning for four various heavy oil samples with viscosities ranging from 100 to 50,000 mPa·s. The presence of all major hydrocarbon components both in crude oil and in each of its fractions was established quantitatively using NMR spectroscopy. Contribution of SARA fractions in the aliphatic (10-60 ppm) and aromatic (110-160 ppm) areas of the ¹³C NMR spectra were identified. Quantitative fractions of aromatic molecules and oil functional groups were determined. Aromaticity factor and the mean length of the hydrocarbon chain were estimated. The obtained results show the feasibility of ¹³C NMR spectroscopy for the express analysis of oil from physical properties to the composition of functional groups to follow oil treatment processes.

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Article

Qualitative and Quantitative Analysis of Heavy Crude Oil Samples and Their SARA Fractions with ^{13}C Nuclear Magnetic Resonance

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Abstract: Nuclear magnetic resonance (NMR) approaches have unique advantages in the analysis of crude oil because they are non-destructive and provide information on chemical functional groups. Nevertheless, the correctness and effectiveness of NMR techniques for determining saturates, aromatics, resins, and asphaltenes (SARA analysis) without oil fractioning are still not clear. In this work we compared the measurements and analysis of high-resolution ^{13}C NMR spectra in $B_0 \approx 16.5$ T (NMR frequency of 175 MHz) with the results of SARA fractioning for four various heavy oil samples with viscosities ranging from 100 to 50,000 mPa·s. The presence of all major hydrocarbon components both in crude oil and in each of its fractions was established quantitatively using NMR spectroscopy. Contribution of SARA fractions in the aliphatic (10–60 ppm) and aromatic (110–160 ppm) areas of the ^{13}C NMR spectra were identified. Quantitative fractions of aromatic molecules and oil functional groups were determined. Aromaticity factor and the mean length of the hydrocarbon chain were estimated. The obtained results show the feasibility of ^{13}C NMR spectroscopy for the express analysis of oil from physical properties to the composition of functional groups to follow oil treatment processes.

Keywords: ^{13}C NMR spectroscopy; crude oil; oil fraction; quantitative composition; SARA; aromaticity

1. Introduction

Knowledge of the chemical composition of crude oil is necessary both for fundamental research and technological processes [1]. Despite the high efficiency of the available methods of oil separation and concentration of individual classes of compounds, there is a need for instrumental approaches to obtain additional detailed information about the structure and properties of the obtained fractions, in addition to characterizing complex oil systems in situ [2,3]. Unless modern tools of in-depth analysis are developed and exploited, information about the nature of oils, and products of their fractioning and processing, remain incomplete.

Use of radiospectroscopic techniques such as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) [4], and their double (NMR and EPR) resonance combinations [5,6] in high magnetic fields ($B_0 > 1.5$ T) have greatly expanded the possibilities for the selective detection of oil structural fragments and functional groups mainly due to the higher spectral resolution.

NMR spectroscopy is based on the phenomenon of resonance absorption of the energy of a radiofrequency (in the frequency range of about $f_{RF} = 1\text{--}1000$ MHz) electromagnetic field due to atomic nuclei having a non-zero magnetic moment. Absorption frequencies depend on the isotopic species of the atom and, for a given isotope, on the position of the atom in the molecule, i.e., its spatial and electronic environment. Initially, NMR belonged to the realm of physics but after the discovery of the chemical shift (i.e., nuclei in different chemical surroundings have different resonance frequencies) the technique quickly became highly important as an analytical tool in chemistry [7–11]. The development of stronger magnets and of multidimensional NMR methods allowed its entry into the field of biology. As a result of its continuously increasing importance in modern chemistry, biochemistry, and medicine, three Nobel Prizes for NMR followed in 1991 (Richard Ernst), 2002 (Kurt Wuthrich), and 2003 (Lauterbur, Mansfield). NMR spectroscopy has also been known to be used for the characterization of petroleum components since 1959 [12–18].

The significance of this unique spectral analysis in terms of efficiency lies in the fact that it allows not only the determination of the structure of complex natural molecules, but also to determine their three-dimensional structure. This is achieved due to the fact that each spectrum contains a large amount of information, akin to the fingerprint of a molecule in the form of frequency lines that are stored in a database.

The main advantage of NMR in comparison with other types of spectroscopy is the possibility of transforming and modifying the nuclear spin Hamiltonian at the will of the experimenter practically without any restrictions and adjusting it to the special requirements of the problem to be solved [19–23]. Due to the great complexity of the picture of not fully resolved lines, many infrared and ultraviolet spectra cannot be deciphered. However, in NMR, transforming the Hamiltonian in such a way that the spectrum can be analyzed in detail makes it possible, in many cases, to simplify complex spectra. The ease with which it is possible to transform the nuclear spin Hamiltonian is due to a number of reasons. Because nuclear interactions are weak, strong perturbations can be introduced, sufficient to suppress unwanted interactions. In optical spectroscopy, the corresponding interactions have a much higher energy and such transformations are virtually impossible. The modification of the spin Hamiltonian plays an essential role in many applications of one-dimensional NMR spectroscopy. At present, the simplification of spectra or an increase in their information content with the help of spin decoupling, coherent averaging by multi-pulse sequences, rotation of samples, or partial orientation in liquid crystal solvents has become widespread [24–27].

Using NMR, it is possible to analyze the chemical nature of individual types of hydrogen and carbon atoms, in various and complex mixtures of petroleum and in the final products obtained by refining processes [28–30]. In the NMR spectra, the functional groups of aromatics, aliphatics, and olefins are well illustrated; accordingly, it is possible to differentiate a polynuclear aromatic from a mononuclear aromatic and to identify the fuel physical properties by the concentration of aromatics and the chain length of aliphatics. ^1H NMR spectroscopy can be applied to the characterization and identification of crude oil fractions, and is a suitable means of predicting the total hydrogen content and the distribution of hydrogen among functional groups present in crude oil. Conversely, suitable information about the molecular carbon skeleton can be obtained by ^{13}C NMR. For these reasons ^{13}C NMR has become one of the most important methods in the analysis of crude oil fractions [31–33].

Interest in the determination of SARA (saturates, aromatics, resins, and asphaltenes) components directly from the ^{13}C NMR experiments is also governed by possibilities to enhance the NMR signal in heavy oils through dynamic nuclear polarization (DNP) by applying EPR to the native for oil [6,34–37] or artificially introduced [38] paramagnetic centers. It was shown that ^1H NMR signal enhancement depends not only on the type, electronic properties, concentration of paramagnetic species, and viscosity of oils but also on the SARA fraction [6,34] that can be selected in situ by choosing an appropriate repetition time of NMR experiment. To the best of the authors' knowledge, all of the oil DNP measurements to date have been conducted on ^1H nuclei. Obviously, as in the case of other NMR/DNP

applications for biological investigations and material science [39], one should expect the rapid development of ^{13}C DNP for oil studies.

Although attempts to find a correlation between the SARA analyses and NMR measurements have been undertaken for some time, in a well-known paper on this topic [19] it is emphasized that “the results cannot be generalized for other samples. To do that, it is mandatory to incorporate a wider range of experimental data of crude oils characterization and their respective” fractions.

Our current work presents the new results of a comprehensive investigation of samples of four crude oils and their sixteen SARA fractions to obtain data on structural group composition using quantitative ^{13}C NMR spectroscopy in the magnetic field of $B_0 \approx 16.5\text{ T}$ ($f_{\text{RF}} = 175\text{ MHz}$). Information on the content of general functional groups obtained by ^{13}C NMR spectroscopy can be useful for fast prediction of oil product properties that change under different types of treatment, in addition to the development of a fingerprinting approach.

2. Materials and Methods

For the current investigation we took four heavy (viscous) oils of various origin and their four SARA fractions (a total of 20 samples). A list of the studied samples and the viscosities of the initial oil is presented in Table 1.

Table 1. Studied oil samples and the viscosities of the initial oil species.

Sample Number ¹	Viscosity, mPa·s	Origin of Oil
1, 1s, 1ar, 1r, 1as	106	Iraq
2, 2s, 2ar, 2r, 2as	1430	Ambar gatur (Turkmenistan)
3, 3s, 3ar, 3r, 3as	2420	Ashal'cha (Republic of Tatarstan, Russia)
4, 4s, 4ar, 4r, 4as	49,700	Cuba

¹ s—saturated compounds, ar—aromatics, r—resins, as—asphaltene fraction.

2.1. SARA Fractionation

According to the ASTM 2007 standard, oil samples were divided into their fractions: saturates, aromatics, resins, and asphaltenes (SARA). Asphaltenes were separated from oils by precipitation with heptane (40:1) for 24 h and subsequent purification from maltenes (saturate, aromatic, and resin) in a Soxhlet extractor [40,41]. The results of SARA analysis of all studied oil samples are reported in Table 2. The analytical parameters, tools, and separation conditions for conducting SARA analysis are shown in Table 3.

Table 2. SARA analysis (%) of studied oil samples.

Sample Number	1	2	3	4
Saturates, %	59.6	73.7	26.2	31.0
Aromatics, %	26.7	14.3	40.6	39.2
Resins, %	12.1	9.8	28.5	14.2
Asphaltenes, %	1.6	2.2	4.7	15.6

Table 3. The analytical parameters, tools, and separation conditions for conducting SARA analysis.

Parameter	Details
sample size	1 g of oil
precipitation of asphaltenes (fold amount of n-alkane)	1:40 heptane
time of precipitation	24 h
temperature of precipitation	room temperature
filtration paper	2.5 μm filter

Table 3. Cont.

Parameter	Details
asphaltene washing	hot heptane
asphaltene extraction	toluene
adsorbent	alumina activated at 430 °C
saturates elution	200 mL of heptane
aromatics elution	200 mL of toluene
resins elution	200 mL of 1:1 toluene-isopropyl alcohol
solvent removal	rotary evaporator

2.2. ^{13}C NMR Spectroscopy

NMR experiments on the initial oil samples (1–4) and their fractions (1s–1as, 2s–2as, 3s–3as, 4s–4as) were performed on a Bruker Avance III HD 700 MHz spectrometer equipped with a quadruple resonance (^1H , ^{13}C , ^{15}N , ^{31}P) QCI CryoProbe. All samples of crude oils and their fractions were diluted in deuterated chloroform (CDCl_3) solvent. Field lock and shimming were achieved using the deuterium signal of CDCl_3 . ^{13}C NMR spectra were recorded using 90° pulses with $11.7 \mu\text{s}$ pulse length and with inverse gated broadband proton decoupling (zgig pulse program); relaxation delay between pulses was 9 s and acquisition time was 3.5 s; spectrum width was set to 220.0 ppm; the number of scans was 3200. An exponential digital filter with the line broadening factor of 10 Hz was applied to process ^{13}C NMR spectra prior to Fourier transformation. Measurements were conducted at the temperature of 30°C . All NMR spectra were integrated after baseline correction, and at least three integration values were taken for each calculation. The relative standard deviation of the results of manual integration did not exceed 3%. The integration of the resonance lines in the ^{13}C NMR spectra was carried out with respect to the ^{13}C signal of the CDCl_3 solvent, for which the value was taken as 1. Estimation of molar fractions of primary (C_p), secondary and quaternary (C_{sq}), tertiary (C_t), aromatic (C_{ar}) carbons, aromaticity factor (F_{CA}), and mean chain length (MCL) of aliphatic hydrocarbons was carried out in a way similar to our previous work (see References [40,42] and data presented in Supplementary Materials).

3. Results and Discussion

The ^{13}C NMR spectra of crude oils 1–4 dissolved in CDCl_3 are shown in Figure 1.

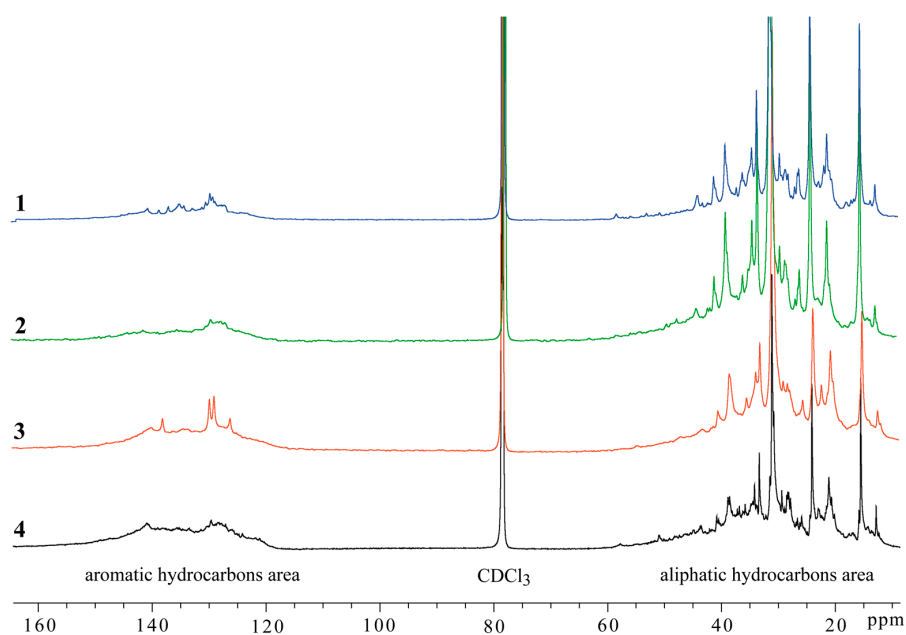


Figure 1. ^{13}C (175 MHz) NMR spectra of oil samples 1–4 in CDCl_3 .

The broadening of resonance lines in the aromatic region of the spectrum in the transition from the light oil sample (1) to the heavier oil samples (2–4) is observed. Table 4 shows the results of estimating the molar content of various carbon groups of samples 1–4 made by integration of the corresponding areas of ^{13}C NMR spectra.

Table 4. Molar fractions (%) of primary (C_p), secondary and quaternary (C_{sq}), tertiary (C_t), aromatic (C_{ar}) groups, aromaticity factor (F_{CA}), and mean chain length (MCL) of aliphatic hydrocarbons based on ^{13}C NMR spectra of samples 1–4.

Sample Number	1	2	3	4
C_p	25.8	18.8	21.6	18.8
C_{sq}	53.0	52.6	48.9	36.6
C_t	10.0	13.9	12.8	15.1
C_{ar}	12.5	14.7	19.3	27.5
F_{CA}	0.123	0.147	0.188	0.275
MCL	6.9	9.1	7.7	7.7

A quantitative analysis of the composition of the oil samples studied by NMR showed that as the oil viscosity increases, a decrease of C_p and C_{sq} parameters and increase in C_t and C_{ar} parameters are observed. Moreover, the concentration of aromatic groups (C_{ar}) in heavy oil sample 4 increases almost two times compared to the less viscous oil sample 1. In addition, with increasing viscosity, the aromaticity factor (F_{CA}) shows an obvious tendency to increase.

Figures 2–5 show ^{13}C NMR spectra of saturated, aromatic, resin, and asphaltene fractions of the studied oil samples. There is also a trend towards broadening of resonance lines in the aromatic area of the spectrum in the transition from the light saturates fraction to the heavier fractions. Quantitative data on the proportions of primary, secondary, tertiary, quaternary, and aromatic carbon atoms of the studied oil fraction samples were also obtained and are presented in Tables 5–8.

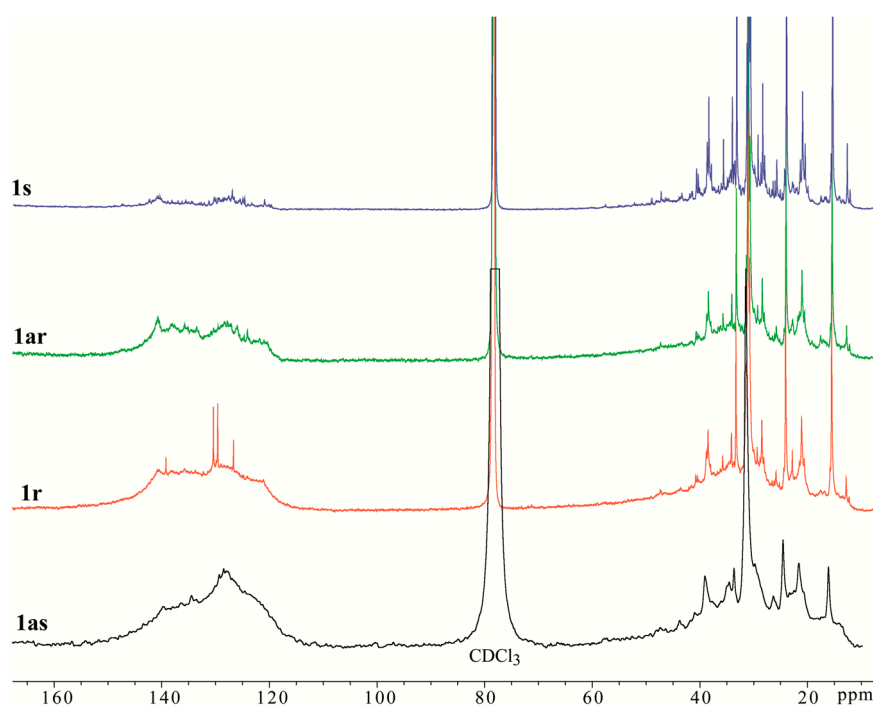


Figure 2. ^{13}C (175 MHz) NMR spectra of oil samples 1s–1as (s—saturated compounds, ar—aromatics, r—resins, as—asphaltene fraction).

Table 5. Molar fractions (%) of primary (C_p), secondary and quaternary (C_{sq}), tertiary (C_t), aromatic (C_{ar}) groups, aromaticity factor (F_{CA}), and mean chain length (MCL) of aliphatic hydrocarbons based on ^{13}C NMR spectra of samples 1, 1s–1as.

Sample Number	1	1s	1ar	1r	1as
SARA fractions, %	crude oil (100%)	saturated compounds (59.6%)	aromatics (26.7%)	resins (12.1%)	asphaltene fraction (1.6%)
C_p	25.8	16.7	12.0	9.5	9.0
C_{sq}	53.0	54.0	40.4	38.7	33.3
C_t	10.0	14.1	13.0	13.1	17.7
C_{ar}	12.5	15.2	34.6	38.7	40.0
F_{CA}	0.123	0.152	0.346	0.387	0.400
MCL	6.9	10.1	10.9	12.9	13.3

Quantitative analysis of the composition of saturated compounds (1s), aromatics (1ar), resins (1r), and asphaltene fraction (1as) of oil sample 1 studied by NMR showed that as the fraction gravity increases, a decrease in parameters C_p , C_{sq} and increase in C_t , C_{ar} , F_{CA} are observed. In addition, with increasing fraction gravity, there is a tendency for the MCL parameter to increase up to 13.3.

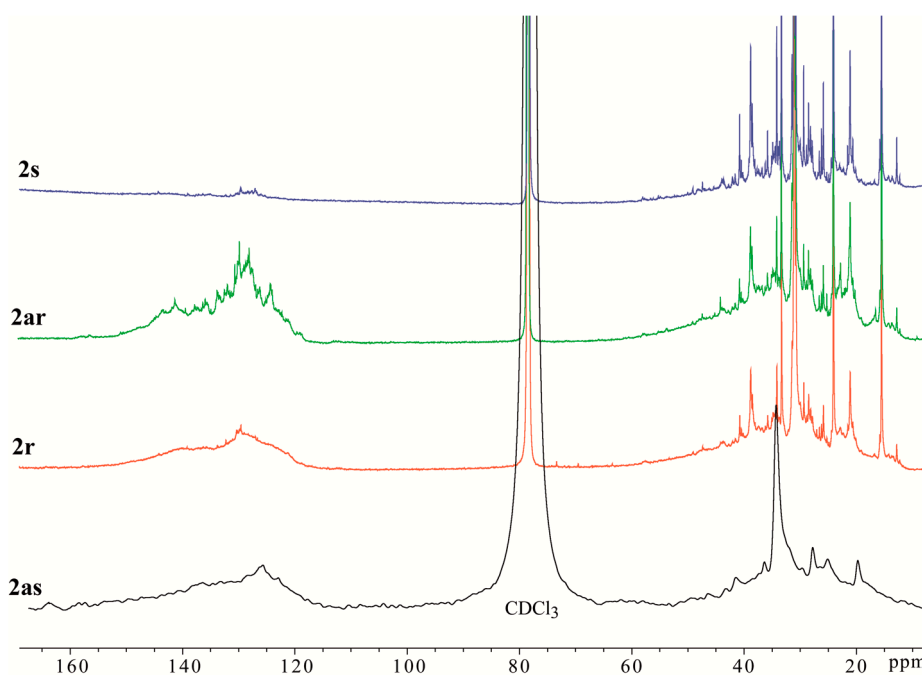


Figure 3. ^{13}C (175 MHz) NMR spectra of oil samples 2s–2as (s—saturated compounds, ar—aromatics, r—resins, as—asphaltene fraction).

Table 6. Molar fractions (%) of primary (C_p), secondary and quaternary (C_{sq}), tertiary (C_t), aromatic (C_{ar}) groups, aromaticity factor (F_{CA}), and mean chain length (MCL) of aliphatic hydrocarbons based on ^{13}C NMR spectra of samples 2, 2s–2as.

Sample Number	2	2s	2ar	2r	2as
SARA fractions, %	crude oil (100%)	saturated compounds (73.7%)	aromatics (14.3%)	resins (9.8%)	asphaltene fraction (2.2%)
C_p	18.8	15.8	11.5	9.5	9.1
C_{sq}	52.6	59.0	45.2	39.2	38.5
C_t	13.9	20.9	16.0	18.0	18.0
C_{ar}	14.7	4.3	27.3	33.3	34.4
F_{CA}	0.147	0.043	0.273	0.333	0.344
MCL	9.1	12.1	12.6	14.0	14.4

Quantitative analysis of the composition of saturated compounds (2s), aromatics (2ar), resins (2r), and asphaltene fraction (2as) of oil sample 2 studied by NMR showed that as the fraction gravity increases, C_p and C_{sq} parameters decrease. However, the concentration of tertiary carbons (C_t) in this case also decreases on average, unlike in the case of sample 1. The concentration of aromatic carbons (C_{ar}) takes the lowest value (4.3%) for the sample of saturates fraction 2s; then, as fraction gravity increases, this parameter evenly increases. In addition, with increasing fraction gravity, there is a tendency for the F_{CA} and MCL parameters to increase.

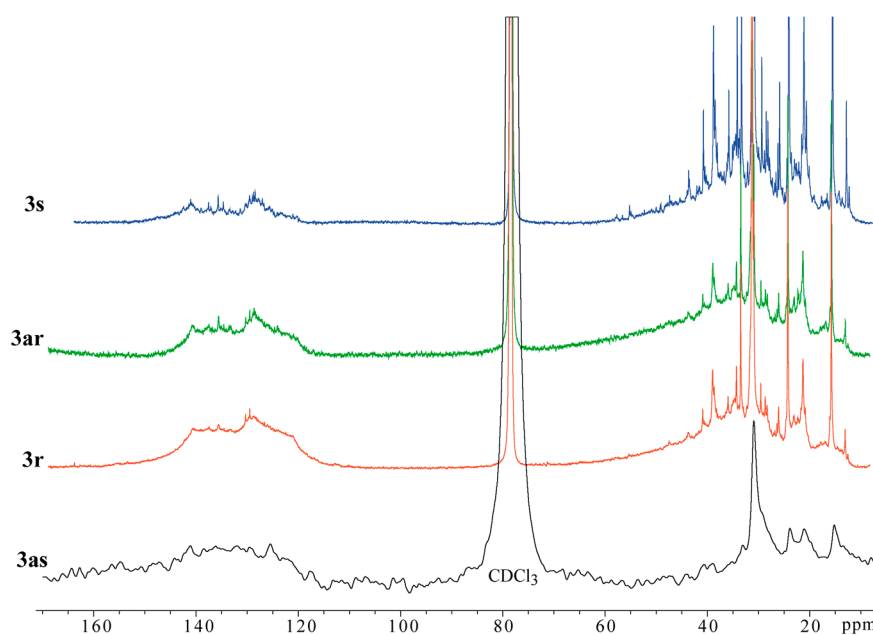


Figure 4. ^{13}C (175 MHz) NMR spectra of oil samples 3s–3as (s—saturated compounds, ar—aromatics, r—resins, as—asphaltene fraction).

Table 7. Molar fractions (%) of primary (C_p), secondary and quaternary (C_{sq}), tertiary (C_t), aromatic (C_{ar}) groups, aromaticity factor (F_{CA}), and mean chain length (MCL) of aliphatic hydrocarbons based on ^{13}C NMR spectra of samples 3, 3s–3as.

Sample Number	3	3s	3ar	3r	3as
SARA fractions, %	crude oil (100%)	saturated compounds (26.2%)	aromatics (40.6%)	resins (28.5%)	asphaltene fraction (4.7%)
C_p	21.6	16.4	12.5	10.2	7.1
C_{sq}	48.9	41.1	41.9	39.4	34.8
C_t	12.8	19.9	20.1	17.2	12.2
C_{ar}	19.3	22.6	25.5	33.2	45.9
F_{CA}	0.188	0.226	0.255	0.332	0.459
MCL	7.7	9.4	11.9	13.1	15.2

Quantitative analysis of the composition of saturated compounds (3s), aromatics (3ar), resins (3r), and asphaltene fraction (3as) of oil sample 3 studied by NMR showed that increasing the fraction gravity is accompanied by a decrease in the C_p , C_{sq} , and C_t parameters and an increase in the parameter C_{ar} . In addition, with increasing fraction gravity, there is a tendency for the F_{CA} and MCL parameters to increase.

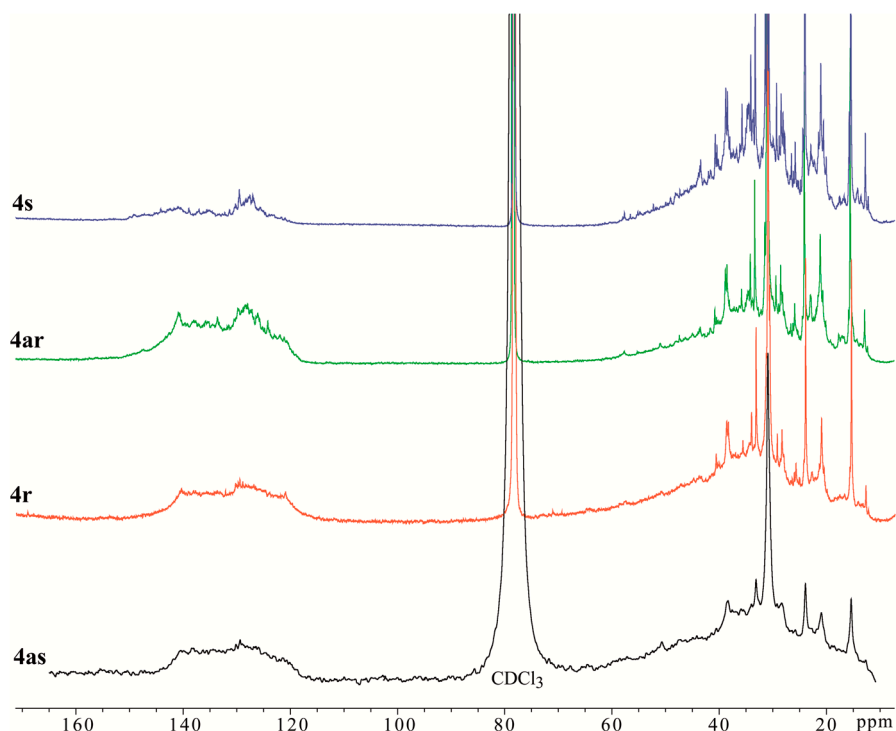


Figure 5. ^{13}C (175 MHz) NMR spectra of oil samples 4s–4as (s—saturated compounds, ar—aromatics, r—resins, as—asphaltene fraction).

Table 8. Molar fractions (%) of primary (C_p), secondary and quaternary (C_{sq}), tertiary (C_t), aromatic (C_{ar}) groups, aromaticity factor (F_{CA}), and mean chain length (MCL) of aliphatic hydrocarbons based on ^{13}C NMR spectra of samples 4, 4s–4as.

Sample Number	4	4s	4ar	4r	4as
SARA fractions, %	crude oil (100%)	saturated compounds (31.0%)	aromatics (39.2%)	resins (14.2%)	asphaltene fraction (15.6%)
C_p	18.8	15.3	13.3	10.7	8.3
C_{sq}	36.6	48.1	46.6	43.0	27.1
C_t	15.1	25.0	26.5	23.9	30.0
C_{ar}	27.5	11.6	13.6	22.4	34.6
F_{CA}	0.275	0.116	0.136	0.224	0.346
MCL	7.7	11.5	13.0	14.5	15.8

The behavior of the studied parameters for the fraction samples of the heaviest oil 4 is the same as for the fraction samples of the lightest oil 1. A quantitative analysis of the composition of saturated compounds (4s), aromatics (4ar), resins (4r), and asphaltene fraction (4as) extracted from oil sample 4 studied by NMR showed that an increase in the fraction gravity correlates with a decrease in parameters C_p and C_{sq} , and an increase in C_t , C_{ar} , F_{CA} , and MCL. Thus, the maximum value of the mean chain length (MCL) equal to 15.8 is observed for the asphaltene fraction of oil sample 4.

Figure 6 shows a summary diagram of changes of the obtained structural group parameters C_p , C_{sq} , C_t , C_{ar} , F_{CA} , and MCL for the studied oil samples. This diagram allows us to analyze how the obtained parameters change according to two criteria: the gravity of the fraction (growing from saturates to asphaltenes) and viscosity of the sample (an increase within the same fraction from sample 1 to sample 4). Thus, for the C_p parameter there is a general decrease of approximately twofold in values as the gravity of the fraction increases. However, analysis of the dependence of the parameter C_p on the sample viscosity among individual fractions shows an ambiguous picture: for saturates and asphaltenes there is a slight decrease in the values of C_p , while for the aromatic and resin fractions the values of C_p slightly increase. A similar trend in changes in individual fractions is observed for the

parameter C_{sq} . However, it was noticed that the reduction in C_{sq} for saturates and asphaltenes as the viscosity of the sample increases occurs more sharply than for C_p . Analysis of the parameter C_t showed that for each fraction its value increases strongly as the viscosity of the samples increases. Furthermore, by the gravity of the fraction increases, there is an increase in C_t values for samples 1 and 4 and a decrease for samples 2 and 3. The behavior of the C_{ar} parameter as the gravity of the fraction increases is exactly opposite to the case of C_p : its values increase sharply. However, its values within individual fractions as the sample viscosity increases have a general tendency to decrease. As an exception to this rule, however, there is a sharp increase in the values of the C_{ar} parameter of sample 3 for saturates and asphaltene fractions. In addition, there is a very sharp drop of the C_{ar} parameter value (down to 4.3%) of sample 2 for the aromatics fraction.

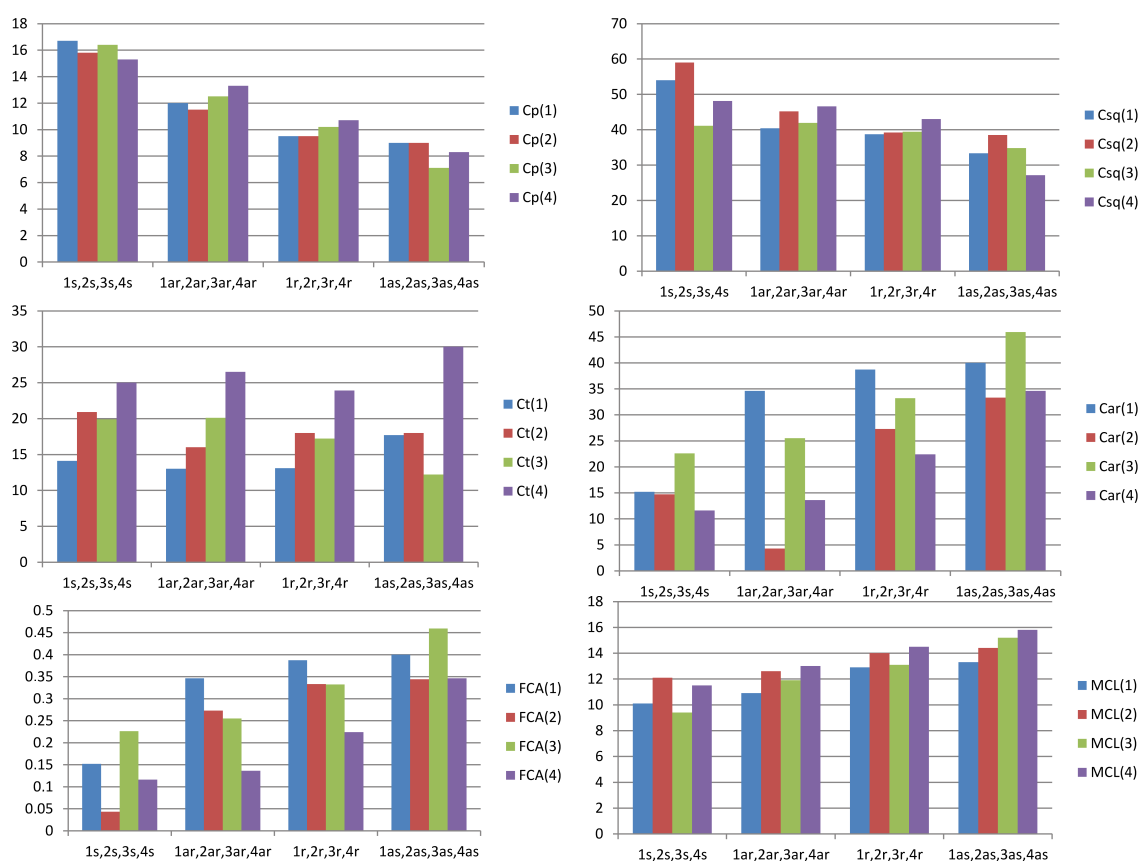


Figure 6. Diagram of changes of obtained parameters C_p , C_{sq} , C_t , C_{ar} , F_{CA} , and MCL for the studied samples of oil fractions.

The remaining parameters—aromaticity factor (F_{CA}) and mean chain length (MCL) of aliphatic hydrocarbons—are indirect. For example, the values of parameter F_{CA} strongly depend on the values of parameter C_{ar} . Therefore, the behavior of its value both with increasing the gravity of the fraction and increasing the sample viscosity within a separate fraction is similar to the behavior of parameter C_{ar} , however, its changes occur more smoothly. The values of the mean chain length (MCL) of aliphatic hydrocarbons, as expected, grow both as the gravity of the fraction and the sample viscosity within a separate fraction increase.

4. Conclusions

^{13}C NMR spectroscopy can significantly expand the repertoire of research methods to study structural-group composition of oil and oil fractions, and adequately describe qualitatively and quantitatively not only the elemental composition but also the molecular structures of natural organic

material, its fractions, and intermediate and target products. These characteristics determine both the properties of objects and the strategy of various technological schemes for oil upgrading or for extraction of different fractions and groups.

Regarding specific results, we determined the contribution of fractions of oil in the aliphatic (10–60 ppm) and aromatic (110–160 ppm) areas of the ^{13}C NMR spectra. We demonstrated that NMR spectroscopy methods make it easy to establish the quantitative presence of the main hydrocarbon components in any fraction of oil. The quantitative fractions of the main functional groups constituting oil hydrocarbons and hydrocarbons of the main oil fractions (saturates, aromatics, resins, and asphaltenes) in several samples were determined and their variations were shown.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/8/995/s1>.

Author Contributions: M.V. and V.K. conceived and designed the research. I.R. and S.E. performed the NMR study. A.A.-M. performed SARA fractionation. I.R., M.G. and V.T. analyzed the data and wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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