

NMR-Spectrometric Determination of the Fragmented Oil Composition from the Karazhanbas and Zhangurshi Oil Deposits

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Abstract

The methods of ¹H, ¹³C NMR-spectroscopy were used to study the fragmentary compositions of oil from the Karazhanbas, Zhangurshi deposits (Kazakhstan) and heavy oil residues obtained before and after the electrohydraulic effect of water hammer after topping a light fraction of oil products. Their fragmentary composition were determined by the value of integrated intensities of ¹H, ¹³C NMR signals of the oil under study. The obtained results have shown that the composition of oil samples under study includes terminal CH₃-groups of long alkyl chains having a value of 0.87 ppm. The presence of long alkyl chains of oil components imparts a high viscosity and bituminous consistency to the latter. The content of aromatic protons according to the integrated intensities of ¹H NMR in both oil samples does not exceed 2.08%; but there are no aromatic nuclei by the integral intensities of carbon atoms at all. The low content of protons of H_α-type in hydrocarbon crude (5.2–5.3%) indicates a low content of aromatic and carbonyl carbons as well as heteroatoms in the studied samples. The content of the greater proportion of protons of the H_γ-type in Karazhanbas oil (33.0%) compared to the Zhangurshi oil (23.8%) indicates a greater length of aliphatic hydrocarbons of the latter and its increased viscosity.

1. Introduction

A modern high-resolution NMR-spectroscopy, being a method of both qualitative and quantitative analysis is widely used to carry out control over the quality of oil and petroleum products [1–5]. The advantage of NMR-spectroscopy in comparison with other methods of oil investigation, such as chromatography, mass spectrometry, optical spectroscopy, is the possibility to obtain the quantitative information without using standard samples and reference substances or mixtures [1, 3]. The usage of NMR-spectroscopy in the analysis of oil and oil products is also demanded within the scope of application of environmentally friendly technologies of “green chemistry”.

Determination of the quality determination of oil and oil products is the most demanded area of

practical analysis. The qualitative indicators of oil and oil products have been laid in their elemental, structural – group, fragmented and compositional analysis, which are “encrypted” in quantitative form in NMR spectra of hydrogen and carbon of oil objects [3]. The knowledge about chemical composition and physical – chemical characteristics of crude oil is necessary for predicting oil refining and quality improvement of obtained oil products, as well as practicability of combining the crude oil from different deposits [3].

The purpose of the study is the NMR-spectroscopic determination of fragmentary oil composition of the Karazhanbas, Zhangurshi deposits as well as heavy oil residue of Kazakhstan obtained before and after the electrohydraulic effect of water hammer after topping a light fraction of oil products.

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2. Experimental

To determine the fragmentary composition, samples of high-tar, high-sulfur crude oil from the Karazhanbas deposit [6] as well as highly viscous, bituminous oil from the Zhangurshi deposit were used.

NMR spectra of ^1H , ^{13}C were taken at 25 °C in deuterated chloroform using JNM-ECA Jeol 400 spectrometer (399.78 and 100.53 MHz on ^1H and ^{13}C nuclei). Chemical shifts are measured in reference to signals of residual protons or carbon atoms of deuterated chloroform.

Description of the installation, experimental procedure, analyses of gas and light fraction of oil sludge are presented in [7–8]. The oil was treated with high-frequency electric discharges in order to increase the output of light fraction with a frequency of 1 electrohydraulic effect per second.

Gas fraction analysis was performed on a gas chromatograph “CHROMOS-1000” with a thermal conductivity detector, carrier gas velocity (Ar) was 20 ml/min, H_2 , N_2 , O_2 were determined using phases of the composition CaA, column length – 2 m, $d = 3$ mm, $T = 350$ °C. For the determination of CO , CO_2 and hydrocarbons using the phases of the composition of AG-3, the velocity of the carrier gas (H_2) was 20 ml/min, $T = 250$ °C. Analysis of the gas fraction for determination of hydrocarbons was performed on the second chromatograph “Chromos-1000” using a capillar column HP-FFAP with the length of 50 m, the velocity of gas-carrier (H_2) was 5 ml/min, $T = 250$ °C, with the flame-ionization detector. In the composition

of the gas fraction, N_2 , CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $\text{iso-C}_4\text{H}_{10}$ and methanol were found.

The liquid fraction was analyzed on an “Agilent Technologies 6890” chromatography mass spectrometer. The detector is mass spectral. Carrier gas is helium, capillary columns are № J&N 122-1232 and Agilent 19091z-105 HP-1. The liquid fraction consists of paraffins, isoparaffins, aromatic hydrocarbons, naphthenes and ether compounds.

3. Results and discussion

To determine the fragmentary composition of oil by the NMR spectroscopy method, the spectrum ^1H and ^{13}C of oil and oil products is divided into several ranges of chemical shifts corresponding to different molecular fragments.

The work [9] presents fragmentary-structural correlations of the oil and oil products according to chemical shift ranges of ^1H , ^{13}C NMR spectra which were proposed by 12 researchers from 1975 to 1994.

In all studies, the proton range of chemical shifts of the oil covers a range from 0.5 to 9.0 ppm, the considered carbon range of chemical shifts has a difference in selected areas: the most considered range is from 0 to 193 ppm. Considering the fact that the sensitivity of proton spectra is 100 times greater than that carbon ones, the greatest information in NMR-spectra of the oil can be obtained according to the ^1H spectra.

To determine the fragmentary composition of the oil under study, we used the ranges of chemical shifts of ^1H and ^{13}C NMR for oil products proposed by G.A. Kalabin and colleagues [1, 10].

Table 1
Ranges of chemical shifts of ^{13}C NMR of petroleum products [1]

Range δ (^{13}C), ppm	The designation of carbon atoms	Signal assignment
7-65	C_{al}	Aliphatic atoms C
7-17	$\text{C}_{\text{p,n}}$	Carbon atoms of CH_3 -groups associated with the methylene group
17-25	$\text{C}_{\text{p,i}}$	Carbon atoms of the CH_3 -groups bound to the CH-group or aromatic ring
17-50	$\text{C}_{\text{s+q}}$	Secondary and quaternary aliphatic atoms C
25-50	C_{Q}	Quaternary aliphatic atoms C
25-65	C_{CH}	Carbon atoms of CH groups
108-118	$\text{C}_{\text{ta,oph}}$	Tertiary aromatic carbon atoms in ortho-position to ethereal oxygen
110-135	C_{ta}	Tertiary atoms of C aromatic system
130-137	C_{ma}	Methyl-substituted aromatic carbon atoms
137-148	$\text{C}_{\text{al,na}}$	Alkyl and naphthyl substituted carbon atoms of aromatic nuclei
148-170	$\text{C}_{\text{al,nan}}$	Alkyl and naphthyl substituted carbons of aromatic nuclei
170-200	C_{c}	Carbonyl carbon atoms

The researchers under the leadership of G.A. Kalabin have conducted a large series of works on the study of the Russian oil using modern high-resolution NMR-spectrometers with superconducting magnets JNM-ECA 600 and JNM-ECX 400 (Jeol, Japan) [11].

Table 1 present some important ranges of chemical shifts of the proton and carbon spectra, with corresponding functional groups assigned to them.

Having integrated the spectral regions of ^1H and ^{13}C NMR (Figs. 1 and 2), it was determined the fragmentary composition of oil (Table 2).

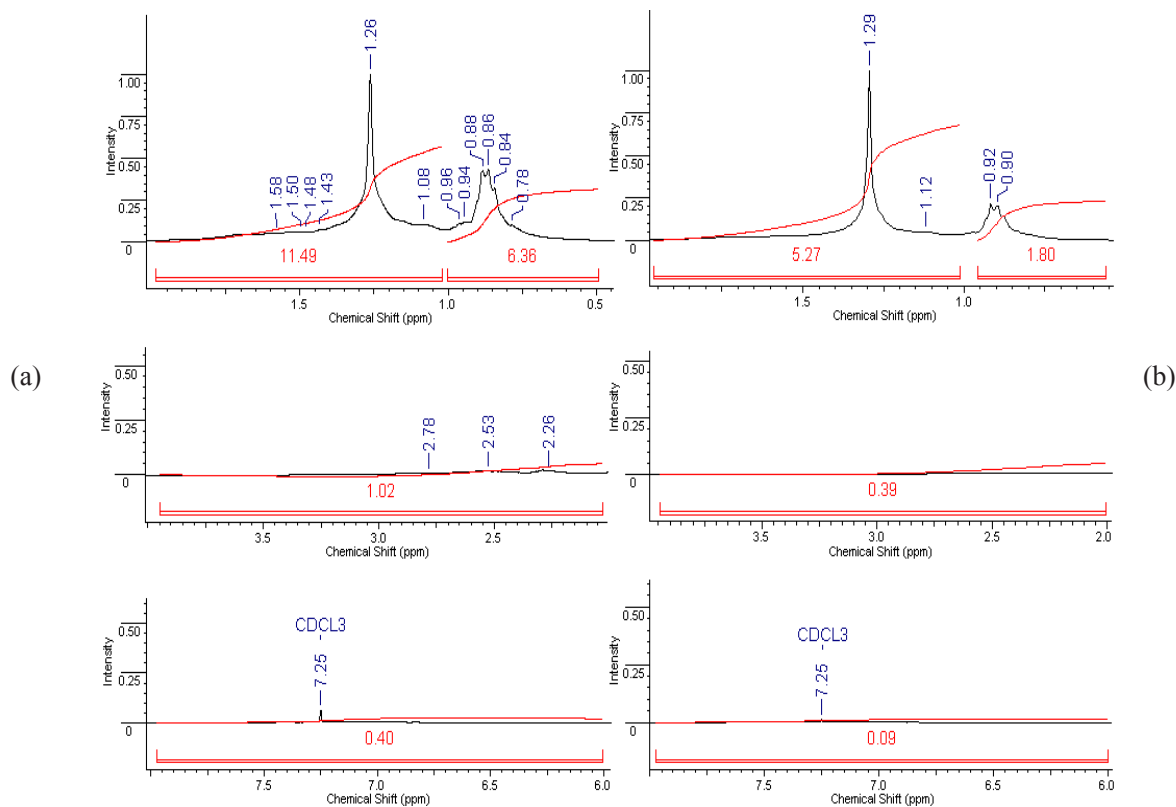


Fig. 1. The integrated sections of the ^1H NMR spectra of the oil of the Karazhanbas field (a) and Zhanggurshi field (b).

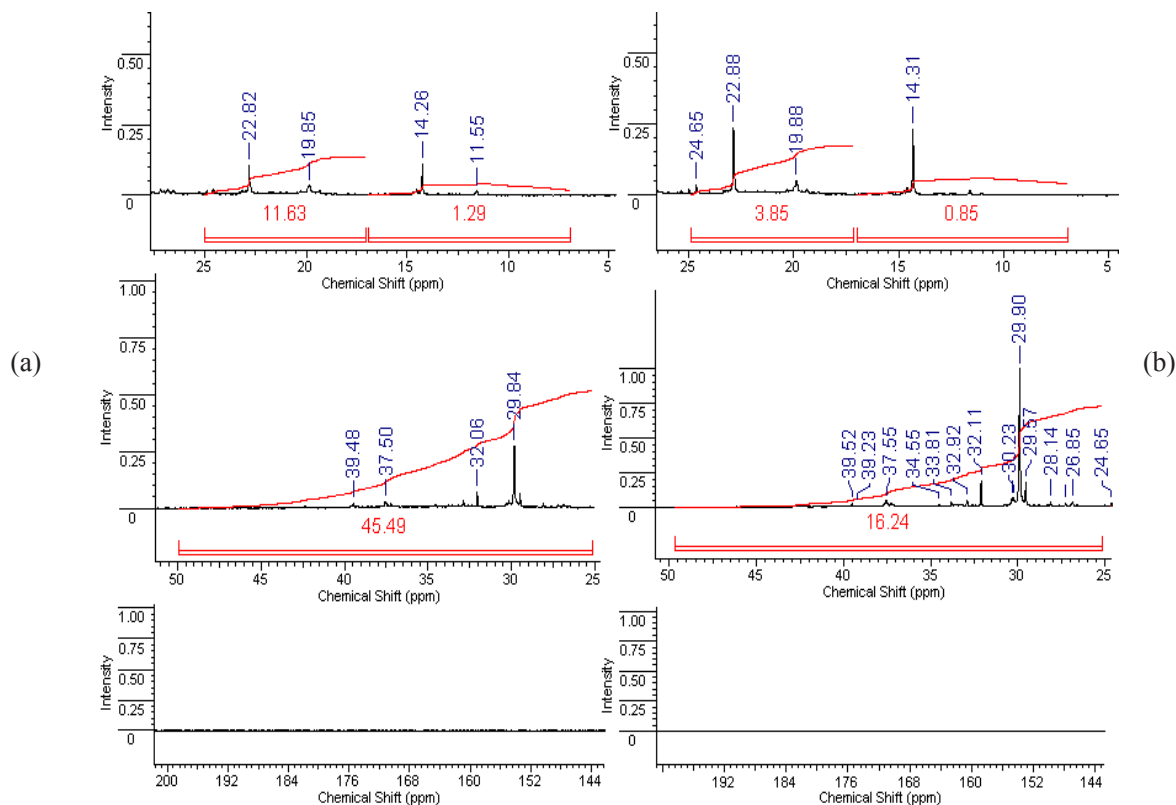


Fig. 2. The integrated sections of ^{13}C NMR spectra of the oil of Karazhanbas field (a) and Zhanggurshi field (b).

Table 2

Fragmentary composition of Karazhanbas and Zhangurshi oil deposits (% mass)

A type atoms	Oil of the Karazhambas deposit	Oil of the Zhangurshi deposit
H _{ar}	2.1	1.2
H _{ol}	0	0.
H _{al}	97.9	98.8
H _α	5.3	5.2
H _β	59.5	69.8
H _γ	33.0	23.8
C _{ar}	0	0
C _{al}	100	100
C _{p,n}	2.2	4.1
C _{p,i}	19.9	18.4
C _{s+f}	97.8	95.9
C _f	77.9	77.5

The obtained results have shown the presence of terminal CH₃-groups of long alkyl chains with a value of 0.87 ppm and in the composition of the oil samples under study. The presence of long alkyl chains of oil components imparts high viscosity and bituminous consistency to the latter. In both samples there are no signals related to the range 4.5–6.3 ppm – characterizing the presence of protons of olefinic nature. Therefore, these parts of the spectra are not presented in Fig. 1. In commercial oils, the content of olefinic hydrocarbons does not exceed 1% [1].

The content of aromatic protons according to the integrated intensities of ¹H NMR in both oil samples does not exceed 2.1%; but there are no aromatic nuclei at integral intensities of carbon atoms at all.

To low content of H_α protons in hydrocarbon crude (5.2–5.3%) indicates a low content of aromatic and carbonyl carbons as well as heteroatoms in the studied samples.

The content of greater proportion of protons of the H_γ-type in Karazhanbas oil (33.0%) compared to the Zhangurshi oil (23.8%) indicates a greater length of aliphatic hydrocarbons of the latter and its increased viscosity.

In general, the considered oil samples are very similar in fragmentation, viscosity and bituminous consistency and can be used for mixing, as well as be subjected to processing under the same technological conditions.

The investigation results by spectral analysis methods of gas and light liquid fractions of the oil products obtained in the course of processing by

electrohydraulic oil shocks differ greatly both in composition and quantity from light fractions obtained without processing of the raw material by electrohydraulic effect which was explained in the previous study [7–8]. The light fractions of oil subjected to the electrohydraulic processing contained 171 hydrocarbon compounds, whereas in similar products without physic-mechanical effect, the number of organic compounds was 161.

The content of ether compounds in light fractions of oil products obtained during electrohydraulic effect of oil is 2 times higher than that obtained without treatment. Electrohydraulic effect on oil allows to increase the yield of gaseous and light liquid fractions of oil products.

NMR-spectroscopic determination of fragmentary composition of heavy oil residue before and after the electrohydraulic effect showed that the composition of heavy oil residuals does not strongly differ in fragmentation.

In original oil, the content of CH₃-groups of saturated compounds, as well as CH₃-groups in aromatic ring, slightly exceeds the content of these groups in oil residue after the treatment and separation of the light fraction

4. Conclusions

A significant increase in the content of methylene and methine groups in the tested samples in comparison with the content of terminal methyl groups indicates the high molecular structure of heavy oil residues. In oil residues, after electrohydraulic effect, the isomeric branched hydrocarbon components do not remain, neither do those subjected to oxidation and aromatization. The content of aromatic fragments in the tested products is insignificant and does not differ much from each other.

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