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Investigation of Electrohydraulic Effect on Physicochemical Characteristics of High-Resinous Oil Karazhanbas

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Abstract

In order to change the viscosity of high-resinous oil of the Karazhanbas field (Kazakhstan), the effect of electrohydraulic (EH) action on it was studied. The effect of adding an organic solvent xylene on the rheological properties of oil is investigated. A comparative study of the hydrocarbon composition of oil before and after electrohydraulic impact was carried out by the method of gas chromatography-mass spectrometry. Fragment composition of oil hydrocarbons before and after electrohydraulic treatment was determined by ^{1}H and ^{13}C NMR spectroscopy. It is shown that the conversion of heavy oil fractions to light ones begins with a five-time electrohydraulic impact. It is determined that 20–25 electric discharge pulses are sufficient for the quantitative process of splitting hydrocarbons. It was found that the addition of xylene to high-viscosity oil leads to an increase in the conversion of hydrocarbons under electrohydraulic action. The content of paraffins and naphthalenes in high-viscosity oil is slightly reduced during electrohydraulic processing. In oil, after electrohydraulic action, a decrease in the proportion of protons of long alkyl terminal CH_3-groups of hydrocarbons is observed, which indicates the process of decomposition of heavy oil fractions into light fractions.

1. Introduction

At present, almost all the growth in the world's proven hydrocarbon reserves is accounted for by "unconventional oils" – high-viscosity bituminous (HVB) and shale oils (ShO), natural oil bitumen (NBO) and oil-bituminous rocks (OBR). Their proven reserves amount to about one thousand billion tons. Therefore, about 30% of the total mass of annual energy supplies to the world oil market is naturally occupied by unconventional oils. Kazakhstan, which ranks 10th in terms of confirmed oil reserves, has a larger reserve of unconventional oil. These include the highly paraffinic and resinous oil Karazhanbas we are investigating (the paraffin content is 21.4 wt%), (the asphaltene resin content is 3.56 and 1.59 wt%, respectively) [1, 2].

The high content of heavy hydrocarbons in high-viscosity oil causes it to solidify at room temperature after extraction from the well. When pumping such oil, hydraulic pressure increases on the main oil pipelines, and paraffins and resins settle on the surface of the transported equipment, leading to a sharp deterioration in its performance.

Among the few methods that allow changing the viscosity of high-viscosity oils, currently one of the most effective is the method of cavitation treatment of hydrocarbon raw materials [3–7]. The use of a pulsed electric discharge – an electrohydraulic (EH) effect-as a source of cavitation can create a highly destructive force that leads to the breaking of both intermolecular and intramolecular chemical bonds. If at the initial stages of cavitation, the destruction of structured oil sections occurs, then with an increase in the intensity and time of the process, the hydrocarbon chains break. The addition of low-molecular organic solvents to the

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oil increases the effect on cavitation. The addition of a solvent contributes to the dilution of oil, and the conversion of high-molecular hydrocarbons in the above-mentioned systems is significantly enhanced.

All of the above prompted us to study the impact of EH impact, as well as the impact of xylene addition on changes in the physical and chemical properties of high-viscosity oil from the Karazhanbas field in the Republic of Kazakhstan.

The aim of this work was to establish the patterns of changes in physico-chemical properties of oil and petroleum products when exposed to high voltage short pulsed electrohydraulic discharge to optimize their processing.

2. Experimental

The main requirements for the experiment were as follows: to accumulate a given amount of energy with its impulse supply to the working interval; significantly reduce the pulse duration and prevent the occurrence of oscillatory processes; create a steep front of the pulse; to exclude the possibility of transition to an arc discharge; to obtain, for a given main interelectrode gap, any of the current and voltage values acceptable for the used power source; regulate the length of the forming gap; change the shape of the pulse and the nature of the discharge at the working gap in the liquid.

Rheological studies of highly paraffinic oil were performed on a rotational viscometer Polymer RPE-1M.2 using a measuring system. This system allows measurements with adjustable shear stress and the shear rate at temperatures from 20 to 60 °C. The relative measurement error of the viscometer does not exceed 4%. Before preparing for testing, the samples were thermostated under static conditions for 30 min.

The description of the installation, the method of conducting the experiment, and the analysis of gas fractions and light fractions of oil are described in [8]. At the beginning of the experiment, the effect of the number of discharges on the depth of the conversion of oil products was established. It was found experimentally that almost 20 pulses are sufficient for the conversion processes to occur. When the number of discharges is less than 5, electrohydraulic action manifests itself rather weakly, and above 30–35, oil coking is observed, i.e. formation of particles of elemental carbon. It was these criteria that determined the boundary conditions for the experiment.

Analysis of the liquid fractions was performed on a gas chromatography-mass spectrometer Agilent Technologies 6890. The 0.5 ml oil samples were diluted in a 1:1 ratio with chloroform and transferred to 2 ml glass vials with plastic screw caps and ultra-clear Teflon/silicone gaskets. The samples were then analyzed by gas chromatography-mass spectrometry (GC/MS).

Using a micro-sample for the Combi-PAL autosampler (CTC Analytics, Switzerland), the sample was inserted into a gas chromatograph sample input device with a mass spectrometric detector 6890N/5973N (Agilent, USA) with a volume of 1 μl in a 10:1 flow division mode. Chromatographic analysis was performed using a 30 m long DB-5MS capillary column with an internal diameter of 0.25 mm and a film thickness of 0.25 microns.

The ^{1}H and ^{13}C NMR spectra of oil samples were taken before and after exposure to an EG discharge and the addition of a small amount of solvent at 25 °C in deuterated chloroform using a JNM-ECA Jeol 400 spectrometer (399.78 and 100.53 MHz at ^{1}H and ^{13}C cores). Chemical shifts are measured relative to the signals of residual protons or carbon atoms of deuterated chloroform.

3. Results and discussion

The results of the EH impact on the oil of the Karazhanbas field showed that structural changes and conversion of oil into light fractions of hydrocarbons begin with a five-time pulsed electric discharge. Twenty times the impact of a pulse discharge leads to an intensification of the oil conversion process.

The quantitative flow of the conversion processes are sufficient for 20–25 pulses of electrical discharge. The values of the initial dynamic viscosity, and the dynamic viscosity after treatment with different amounts of EH oil discharges are presented in Table 1.

The results indicate that the impact of EH discharges leads to a slight decrease in the dynamic viscosity. An increase in the intensity of the EH discharge also leads to a slight decrease in the oil viscosity. Data on changes in the dynamic viscosity of oil after diluting it 5–10% by volume with organic xylene, as well as processing them with 25 EH discharges are presented in Table 2.

From the data in Table 2, it can be seen that dilution of oil with an organic solvent in the range of 5–10% by volume leads to a significant decrease in the dynamic viscosity to almost half in comparison with the source oil. The gas chromatography-mass spectrometry method was used to determine the component composition of the initial oil and oil after dilution with xylene and EH exposure (Fig. 1).

Table 1

Dynamic viscosity oils of Karazhanbas oil field before and after electrohydraulic (EH) treatment at 20 °C

#	Sample	Dynamic viscosity (Pa·s) at the shear rate (s^{-1})	
		3.8	7.6
1	Initial oil	1.76	1.58
2	Oil after treatment with 10 discharges	1.62	1.54
3	After preliminary homogenation and EH treatment with 25 discharges	1.61	1.52

Table 2

Dynamic viscosity oils of Karazhanbas oil field with addition of solvent xylene after electrohydraulic (EH) treatment at 20 °C

#	Sample	Dynamic viscosity (Pa·s) at the shear rate (s^{-1})			
		3.8	7.6	15.1	30.2
1	Initial oil	1.76	1.57	1.49	1.44
2	Oil with 10 vol.% of xylene	0.80	0.75	0.73	0.71
3	Oil with 10 vol.% of xylene after EH treatment	0.11	0.04	0.03	0.03
4	Oil with 5 vol.% of xylene	1.00	0.97	0.95	0.93
5	Oil with 5 vol.% of xylene after EH treatment	0.39	0.35	0.35	0.34

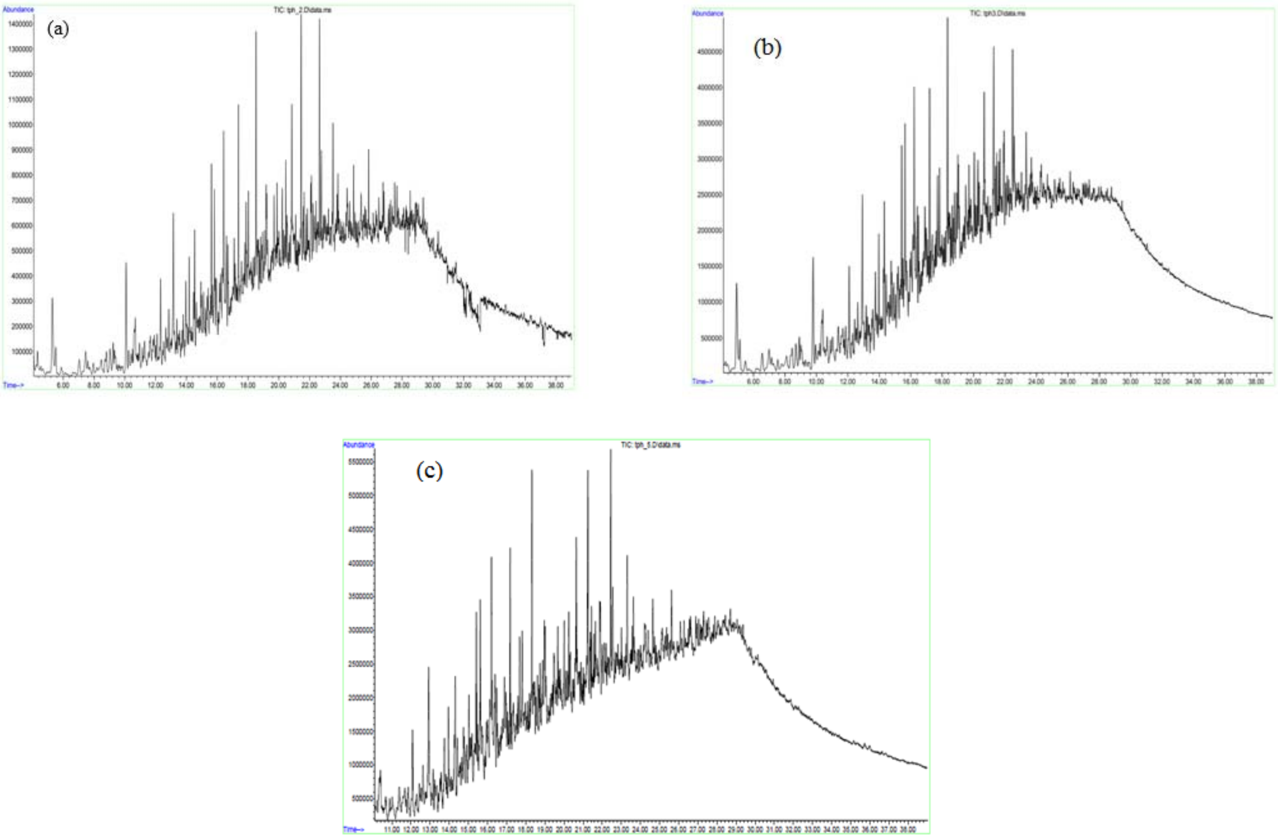


Fig. 1. The chromatogram of the initial oil of Karazhanbas oil field (a), the oil after EH treatment (b) and the oil with addition of 5% xylene and EH treatment (c).

The obtained chromatograms and mass spectra were processed using the automated program Petrol Analysis, which allows determining the component composition of oil for 11 groups of hydrocarbons. Previously, this program was successfully tested when determining the component composition of oil and oil-contaminated facilities in Kazakhstan [9]. The results on the component compositions of the initial oil, oil after its treatment with EH exposure, as well as dilution with xylene and treated with EH impacts, calculated using the Petrol Analysis program, are presented in Table 3.

Table 3
The component composition of oil of Karazhanbas oil field, % wt.

#	Oil components	Oil		
		Initial	After EH treatment with 25 discharges	With 5 vol. % of xylene after EH treatment with 25 discharges
1	Paraffins	15.95	14.14	14.98
2	Non-condensed cycloparaffins	17.40	18.46	18.23
3	Condenced cycloparaffins with 2 rings	14.56	16.15	16.27
4	Condenced cycloparaffins and all cycloparaffins with 3 rings	11.97	12.63	12.44
5	Benzenes	9.48	9.34	9.36
6	Naphthenobenzenes	5.63	5.57	5.37
7	Dinaphthenobenzenes	5.57	4.97	4.78
8	Naphthalenes	6.86	5.87	5.84
9	Acenaphtenes	4.91	4.74	4.74
10	Fluorens	4.91	5.00	4.96
11	Phenanthrenes	2.76	3.15	3.03

Table 3 shows that the percentage of paraffins and naphthalenes decreased slightly during EH oil processing. Minor changes in the content are also observed for other components when diluting the oil with xylene and EH exposure. The greatest contribution to the change in the component composition of the oil is also made by adding 5% by volume of xylene solvent.

Data on the individual composition of petroleum hydrocarbons determined by gas chromatography-mass spectrometry showed insignificant changes in their quantity. Thus, there are 100 types of individual compounds in the source oil, and 95 names of compounds were found in the oil after the EH with 25 discharges. When diluting 5% by volume of oil with xylene and subsequent exposure to EH, the number of compounds increases to 110 compounds. Quantitative data on the substances found in the largest amounts in the source oil and products after EH exposure and xylene dilution are presented in Table 4.

The received results for 8 compounds present in oil show insignificant changes in their content in products after dilution with xylene and treatment with EH exposure. This can serve as an indicator of the progress of processes with the destruction of intermolecular and intramolecular bonds in high-viscosity oil during cavitation by its EH action.

Table 4
The content of individual compounds in oil, % wt.

#	Compounds	Oil		
		Initial	After EH treatment with 25 discharges	With 5 vol.% xylene after EH treatment with 25 discharges
1	1,1,3-trimethylhexane	3.8917	3.7068	1.9139
2	1,1-dimethyl-2-propylcyclohexane	2.0297	2.0370	3.0794
3	Decahydronaphthalene	3.3075	2.8719	1.6985
4	2-methyl-trans-decalin	1.7872	1.6220	2.0569
5	1-Butyl-2-propylcyclopentane	1.7033	1.2335	0.7649
6	2,6,10-trimethyldodecane	2.6514	2.9204	2.6516
7	2,6,10,14-tetramethylpentadecane	3.2992	4.1943	4.0427
8	2,6,10,14-tetramethylhexadecane	2.6520	3.9146	3.4638

Table 5
The ranges of chemical shifts of ^{1}H petroleum products NMR [8]

δ(^{1}H), ppm	Atom designation	Functional group
0.5-1.0	H_γ	CH_3 – groups of saturated compounds. CH_3 – groups in γ- and farther positions to the aromatic ring.
1.0-2.0	H_β	CH_2 and CH groups of saturated compounds. Hydrogen atoms of β-methyl, β- and farther methylene and methine groups at the aromatic ring.
2.0-4.0	H_α	Hydrogen atoms in α-position to aromatic and carbonyl carbons, heteroatoms
4.5-6.3	H_{ol}	Hydrogen atoms of olefin groups
6.3-9.0	$H_{aromatics}$	Hydrogen atoms of aromatic nuclei, phenolic hydroxyls

In order to reveal the correlation dependence of the component composition of the investigated oil with its fragmentary composition, the study of the treated EH by the action of hydrocarbons was carried out by the method of NMR spectroscopy [10–12]. To determine the fragment composition of oil by the method of NMR spectroscopy, the ^{1}H and ^{13}C spectra of hydrocarbons were subdivided into a number of ranges of chemical shifts corresponding to different molecular fragments according to those adopted in [13]. This correlation of the fragmentary structural characteristics of oil and oil products to the ranges of chemical shifts of the ^{1}H and ^{13}C NMR spectra is the most frequently used by researchers in recent years. The proton region of oil chemical shifts covers the range from 0.5 to 9.0 ppm (Table 5), the considered carbon region of chemical shifts included from 0 to 193 ppm. Taking into account that the sensitivity of proton spectra is 100 times higher than that of carbon ones, the greatest information in the NMR spectra of oil can be obtained from ^{1}H NMR spectra.

Figure 2 shows the integrated sections of ^{1}H and ^{13}C NMR spectra of the initial oil (Fig. 2a), oil after EH treatment with 25 discharges (Fig. 2b), oil with 3% (Fig. 2c) and with a 5% xylene content by volume after EH treatment with 25 discharges (Fig. 2d). The fragment composition of the studied oils was determined by integrating the indicated regions of ^{1}H NMR spectra (Fig. 2, Table 6).

The results show that the composition of the oil samples under consideration contains terminal CH_3 groups of long alkyl chains, which appear at a chemical shift of 0.87 ppm. The presence of long alkyl chains of oil components gives the latter a high viscosity and bituminous consistency. In the initial oil and its samples, after exposure to electrohydraulic shock and the addition of a small amount of solvent, there are no signals related to the range of 4.5–6.0 ppm – characterizing the presence of protons of olefinic nature. Therefore, these parts of the spectra in Fig. 2 are not integrated. The content of olefinic hydrocarbons usually does not exceed 1% in commercial oils.

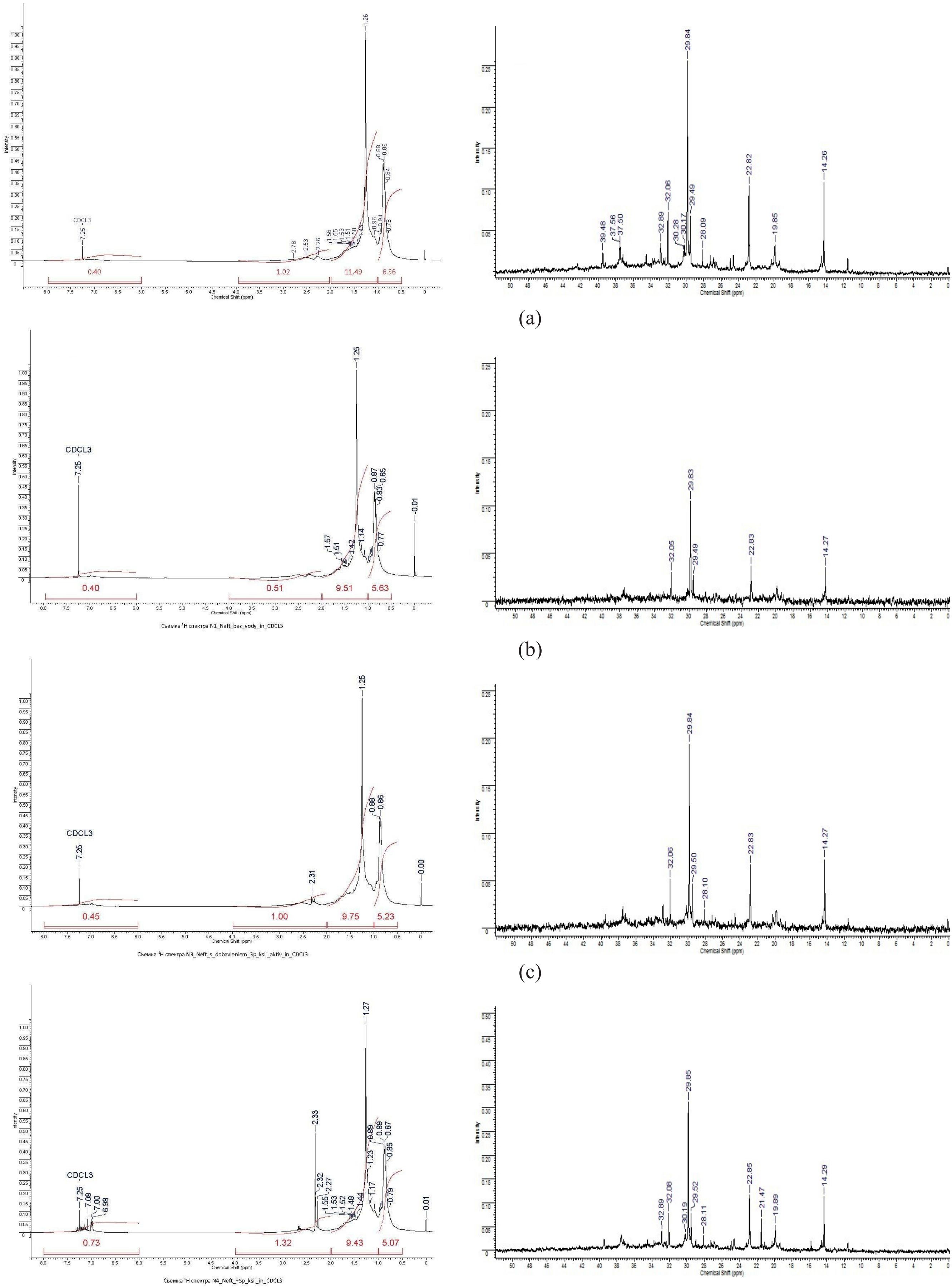
The content of aromatic protons according to the integral intensities of ^{1}H NMR in the source oil does not exceed 2.1%, the impact of EH shock, as well as the addition of xylene oil with subsequent EH discharge leads to an increase in aromatic fragments up to 4.4%. Accordingly, the content of aliphatic compounds decreases in the opposite direction. Aliphatic and alicyclic representatives predominate in a number of individual compounds contained in oils in the largest amount.

The highest content of the H_γ -type proton fraction is observed in oil after electrohydraulic action. This is probably due to a slight break in hydrocarbon chains with an increase in terminal CH_3 groups in oil. This should reduce the viscosity of oil by reducing the length of the hydrocarbon chains.

The results obtained on the ^{13}C NMR spectra of the studied samples of petroleum products (Fig. 2) agree with their ^{1}H NMR data. The results obtained on the ^{13}C NMR spectra of the studied samples of petroleum products (Fig. 2) agree with their ^{1}H NMR data.

Table 6
Fragment composition of oil, % wt.

Type of atoms	Oil		
	Initial	After EH treatment with 25 discharges	With 5 vol.% xylene after EH treatment with 25 discharges
$H_{aromatics}$	2.1	2.5	4.4
H_{ol}	0	0	0
H_{al}	97.9	97.5	95.6
H_α	5.3	3.2	8.0
H_β	59.6	59.3	57.0
H_γ	33.0	35.0	30.6



(d)

Fig. 2. Integral sections of the ^{1}H NMR and ^{13}C spectra of oil: initial (a); after EH processing: 25 discharges (b) and with a xylene content of 3% (c) and of 5 vol.%, 25 discharges (d).

4. Conclusion

It is shown that dilution with xylene and electrohydraulic impact in the amount of 20–25 pulses contributes to a significant decrease in the dynamic viscosity of high-viscosity oils of the Karazhanbas field. Dilution with xylene and exposure to an electrodynamic pulse promotes processes with the destruction of intermolecular and intramolecular bonds in high-viscosity oil. As modern research shows, oil is a dispersed system. Complex structural units (CCE) are the dispersed phase in it. As a result of EH processing, their destruction occurs, the number of molecules per unit volume increases, therefore, the density also increases. Since the size (mass) of these molecular fragments tends to a certain nominal during destruction, the density, as a result, changes insignificantly. When a solvent (xylene) is added, the density of the dispersed phase decreases, which leads to an increase in the destruction of CCE and causes an increase in the yield of fractions boiling in the temperature range of 300–350 °C (diesel distillate oil), as well as the yield of volatile hydrocarbon fractions (up to C6) .

Using gas chromatography-mass spectrometry, it was determined that during electrohydraulic processing of high-viscosity oil, the content of paraffins and naphthalenes in it decreases slightly, and changes in the quantitative values of individual compounds are observed. It was found that the proportion of protons of long alkyl terminal CH_3 groups of hydrocarbons decreases in oil after electrohydraulic action, which indicates the process of decomposition of heavy oil fractions into light fractions.

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