Journal of Siberian Federal University. Chemistry 1 (2011 4) 11-17
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УДК 665.613

# Laboratory Simulation of the Effect of Oil-Displacement Systems on the Composition and Properties of High-Paraffin Crude Oil

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Received 4.03.2011, received in revised form 11.03.2011, accepted 18.03.2011

*The effect of oil-displacement system NINKA on the composition and physical and chemical properties of high-paraffin crude oil was investigated. Prior to testing, the crude oil samples were heated to 200 °C in the presence of NINKA system. It was found that the molecular-mass distribution of hydrocarbons, the sulfur content and density of crude oil had been unaffected by the thermal treatment in the presence of NINKA system; however, the contents of resins and asphaltenes, organic acids and nitrogen had changed significantly.*

*Keywords: high-paraffin crude oil; heavy-viscosity crude oil; oil-displacement system; laboratory simulation; composition; property; saturated and aromatic hydrocarbons; organic acids.*

It is known that the application of EOR methods, e.g. oil-water two-phase flows or oil displacement agents, is liable to cause a change in the composition and physical and chemical properties of recovered crude oil. Thus the fraction of high-viscosity and high-paraffin crude oil would increase, which is the main difficulty for its production, transportation and refining. Besides, the chemical reagents and surfactants present in the oil displacement system would interact with formation fluids, thereby deteriorating the quality of recovered crude oil. Therefore, an in-depth investigation of the effect of oil displacement systems on the composition and properties of recovered oils is a must.

## Experimental

The investigation was carried on for heavy high-viscosity and high-paraffin crude oil produced from a field of Germany.

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Table 1. Physical and chemical characteristics of crude oil from a field of Germany

| | |
|---|---|
| Perforation interval, m | 750-850 |
| Density at +15°C, kg/m$^3$ | 906.0 |
| Dynamic viscosity at +20°C, Pa • s | 1.16 |
| Pore point, °C | +15.3 |
| Boiling point, °C | +76 |
| Percent by mass | |
| Mechanical impurities | 0.5 |
| Sulfur | 1.05 |
| Paraffins | 9.81 |
| Asphaltenes | 0. 3 |

The physical and chemical characteristics of the studied crude oil are listed in Table 1.

The NINKA system was developed for enhanced oil recovery at the Institute of Petroleum Chemistry (Tomsk). This is composed of carbamide, ammonium nitrate and surfactants, the remainder being water. The effect of different surfactants on the composition and properties of crude oil was studied using neftenol VVD, AF 9-12 or neonol NP-50 as an alternative EOR system [1, 2].

Using laboratory simulation, the effect of the above systems on the composition and properties of crude oil was studied. The mixture of crude-NINKA system was used in the volume ratio of 2:1. Prior to testing, each sample of crude-NINKA system mixture was placed in a closed autoclave and allowed to stand for 32 h at constant temperature (200 °C); then it was cooled to room temperature.

The viscosity of crude oil was measured by a vibration method on a viscosimeter unit «Rheokinetics» [3] and its density – by a pycnometer method [4].

The total nitrogen and sulfur contents of crude oil were determined, respectively, by the method of oxidation destruction in NiO layer and by the Schöniger flask method [5].

The individual composition of n-alkanes was investigated by the method of gas-liquid chromatography on a unit 'Chromos GC–1000' equipped with a flame-ionization detector using helium as gas carrier; the capillary column having length of 25 m was coated with SE-54 phase. The chromatograms were recorded using linear temperature programming from 80 °C to 280 °C at a rate of 4 °C per min.

The IR spectra were recorded in thin layer in the region 400 – 4000 cm$^{-1}$ using a Fourier IR unit 'Nikolet 5700' equipped with a Raman module (Thermo Electron Corporation, USA).

The spectroscopic factor, the coefficient C, is the ratio of optical densities (D) of characteristic absorption bands in the IR spectral region, which correspond to respective bond types [6].

The values C were calculated from the following formulae:

$C_1 = D_{1610}/D_{720}$ – the conventional ratio of aromatic to paraffin structures;

$C_2 = D_{1380}/D_{1470}$ – the conventional content of $CH_3$ groups, which characterizes paraffin chain branching;

$C_3 = D_{975}/D_{720}$ – the conventional ratio of naphthene to paraffin structures;

$C_4 = D_{1710}/D_{1470}$ – the conventional content of C=O groups (ketones and organic acids);

$C_5 = D_{1670}/D_{1470}$ – the conventional content of N-H groups (amines and amides of organic acids).

The group composition of crude oil, i.e. saturated and aromatic hydrocarbons, benzene and alcohol-benzene resins, was determined by the method of liquid-adsorption chromatography using silica gel and alumina (2nd degree of reactivity) as sorbent. The asphaltene content was defined chemically as the precipitate formed by the addition to the crude sample of a low-boiling paraffin solvent, e.g. n-hexane.

The total organic acid content was determined by potentiometric titration of the test samples using alcohol alkali solution. The contents (% by mass) of COOH groups (a) and of free organic acids (b) were calculated as follows:

$C_{COOH} = (V_t – V_o) \cdot N_t \cdot 45/10 \cdot m$

$C_k = C_{COOH} \cdot MM / 45$

where: $V_t$ – the volume of potassium hydroxide used for the titration of an analyzed batch to the equivalence point (ml);

$V_o$ – the volume of alcohol alkali solution used for the titration of blank solution (ml);

$N_t$ – the concentration of alcohol alkali solution, mole/l;

45 – the equivalent of COOH-group;

m – the mass of crude oil sample, g;

MM – the molar mass of organic acids (300 $g \cdot mol^{-1}$).

## Results and discussion

The effect of EOR systems on the elemental and functional-group composition as well as on the density and viscosity of crude oils was studied for the test samples of crude-NINKA system mixture, which had been subjected to heat treatment. The results are presented in Table 2.

It was found that the compositions based on neftenol VVD and neonol NP-50 would cause the viscosity of crude oil to decrease, which might be due to its saturation with the $CO_2$ and $NH_3$ gases evolving by carbamide decomposition; the sulfur content and density of crude oil would remain practically the same.

The NINKA system treatment is found to result in a significant increase in the total nitrogen content of the studied crude oil samples. Besides, the treated crude samples are found to contain no free organic acids, which is probably due to crude oil components interacting with the ammonia produced by carbamide decomposition [7].

Using the method of liquid-adsorption chromatography, we determined the group composition of the original crude oil samples and of those treated with the composition. The data obtained is presented in Table 3.

Table 2. Physical and chemical properties and composition of the original and treated crude oils

| Crude oil | Viscosity, Pa • s | Density, kg/m³ | Content, % by mass | | |
|---|---|---|---|---|---|
| | | | $S_{tot}$ | $N_{tot}$ | Organic acids |
| Original crude | 1.16 | 898 | 0.93 | 0.18 | 1.6 |
| Crude oil treated with NINKA (neftenol VVD) | 0.78 | 899 | 0.91 | 0.59 | None |
| Crude oil treated with NINKA (AF 9-12) | 2.13 | 892 | 1.01 | 0.66 | None |
| Crude oil treated with NINKA (neonol NP-50) | 0.86 | 911 | 1.04 | 0.45 | None |

Table 3. The composition of the oil samples studied

| Crude oil components | Content, % by mass | | | |
|---|---|---|---|---|
| | Original crude oil | Crude oil treated with Neftenol VVD | Crude oil treated with AF 9-12 | Crude oil treated with Neonol NP-50 |
| Fraction $T_{bp}$- 200 $^0$C | 25.2 | 3.0 | 11.8 | 7.7 |
| Saturated HCs | 36.2 | 47.7 | 43.9 | 46.5 |
| Aromatic HCs | 21.9 | 26.7 | 22.5 | 22.8 |
| Resins | 12.2 | 15.0 | 17.8 | 17.6 |
| Asphaltenes | 0.3 | 3.1 | 1.6 | 1.5 |
| Saturated/Aromatic HCs | 1.6 | 1.8 | 1.9 | 2.3 |
| Sat. HCs + Arom. HCs/ Resins+Asphaltenes | 7.7 | 5.3 | 5.0 | 5.0 |

It can be seen that the contents of resins and asphaltenes in all the studied samples have increased by 1.2-1.5 and 5-10 times, respectively. The HCs content of the studied samples (fraction $T_{bp}$ – 200 $^0$C) has also changed significantly. Thus the fraction of high-molecular HCs has decreased dramatically and that of saturated and aromatic HCs has increased relative to the original crude oil samples.

The above changes might be due to the fact that the micelles of non-ionogenic surfactants would grow in size with increasing temperature to start interacting with one another. Micelle formation is known to cause solubilization, which plays an important role in a number of processes, both natural and technologic ones [7]. Solubilization is liable to cause partial dissolution in the aqueous phase of light saturated and monoaromatic HCs, with a portion of light HCs evolving in the gaseous form by heating to 200 $^0$C to volatilize completely. Thus, the thermal treatment of crude oil samples using the NINKA system might cause a significant change in the composition of crude oil, in particular, the saturated and aromatic HCs content.

Gas chromatograph used for the analysis of n-alkanes (see Fig. 1).

As is seen from Figure 1 and Table 4, the treatment of the original crude using NINKA systems on the base of different surfactants has caused no significant change in the molecular mass distribution and in the content of light and heavy n-alkanes.

An analysis of the IR data suggests that the treatment of the original crude oil results in the disappearance of the absorption band from the region 1710 cm$^{-1}$. However, the absorption bands observed in the regions 3400-3500 cm$^{-1}$ and 1690-1630 cm$^{-1}$ are characteristic, respectively, of N-H and C=O bond vibrations of amides of organic acids (see Fig. 2).

Upon NINKA system decomposition, the ammonia is liberated to interact with the organic acids of the crude to give amides as suggested by a change in the coefficients $C_3$ and $C_4$ (see Table 5). The coefficients $C_1$ and $C_2$ were calculated from the IR data; the values obtained are indicative of an increase in the total aromatic HCs fraction. The coefficients $C_6$ and $C_5$ were calculated for naphthenic and iso-aliphatic HCs, respectively. The latter values suggest that the fractions of these compounds have changed only insignificantly relative to the normal aliphatic structures.

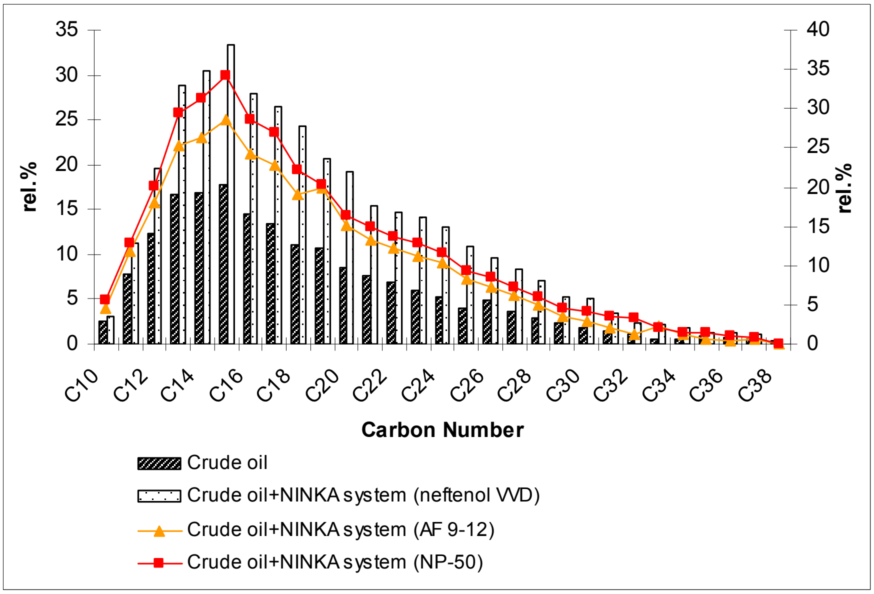


Fig. 1. Molecular mass distribution of n-alkanes of the original and treated crude oil samples

Table 4. Composition parameters of n-alkanes of the original crude and crude oil treated with NINKA system

| Crude oil | $C_{17}/C_{27}$ | Content, % rel. | | |
|---|---|---|---|---|
| | | $C_{15}+C_{17}$ | $C_{21}+C_{23}$ | $C_{27}+C_{36}$ |
| Original crude | 3.72 | 24.93 | 11.18 | 8.84 |
| Crude oil treated with NINKA (neftenol VVD) | 3.14 | 24.26 | 12.23 | 10.59 |
| Crude oil treated with NINKA (AF 9-12) | 3.65 | 24.89 | 12.11 | 8.37 |
| Crude oil treated with NINKA (neonol NP-50) | 3.74 | 25.46 | 11.73 | 9.83 |

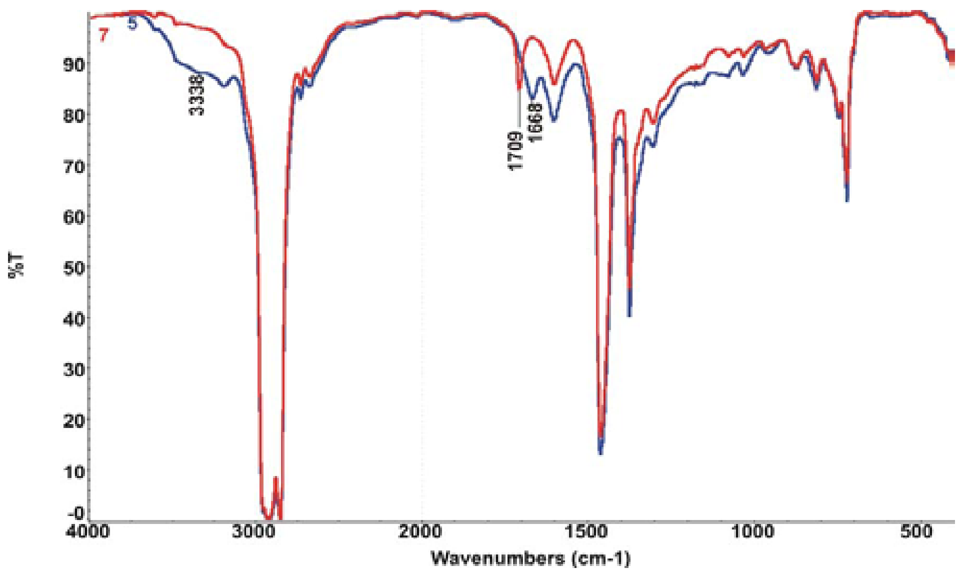


Fig. 2. IR spectra of the original crude oil (7) and of crude oil treated with the composition NINKA (5)

Table 5. Spectral characteristics of the original crude and of the crude oil treated with NINKA system

| Crude oil | $C_1=D_{1610}/D_{720}$ | $C_2=D_{1610}/D_{1470}$ | $C_3=D_{1710}/D_{1470}$ | $C_4=D_{1670}/D_{1470}$ | $C_5=D_{1380}/D_{1470}$ | $C_6=D_{975}/D_{720}$ |
|---|---|---|---|---|---|---|
| Original crude oil | 0.37 | 0.08 | 0.09 | None | 0.43 | 0.18 |
| Crude oil treated with NINKA (AF 9-12) | 0.43 | 0.10 | None | 0.08 | 0.45 | 0.19 |
| Crude oil treated with NINKA (neonol NP-50) | 0.51 | 0.12 | None | 0.09 | 0.45 | 0.18 |
| Crude oil treated with NINKA (neftenol VVD) | 0.55 | 0.13 | None | 0.10 | 0.47 | 0.16 |

## Conclusions

1. The interaction of NINKA system with high-paraffin crude oil at 200 °C results in a decrease in the content of low-boiling HCs, with the distribution of $C_{15} – C_{36}$ n-alkanes remaining the same.
2. The treatment of crude oil using NINKA system brings about an increase in the fraction of saturated and aromatic HCs, with the former compounds prevailing in the treated crude samples.
3. The contents of nitrogen compounds and of resins+asphaltenes would also increase in the treated crude samples.

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# Моделирование в лабораторных условиях влияния нефтевытесняющих композиций на состав и свойства высокопарафинистой нефти

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*Изучено влияние нефтевытесняющей композиции НИНКА на изменение состава и физико-химических свойств высокопарафинистой нефти, которая была подвергнута нагреванию при 200 °С в лабораторных условиях. Установлено, что воздействие композиции не оказало существенного влияния на молекулярно-массовое распределение углеводородов, содержание серы и плотность нефти. Под действием композиции произошло увеличение содержания смолисто-асфальтеновых веществ, органических кислот и азота.*

*Ключевые слова: высокопарафинистые нефти; высоковязкие нефти; нефтевытесняющие композиции; лабораторное моделирование; состав; свойства; насыщенные и ароматические углеводороды; органические кислоты.*