

Influence of Rock-Forming and Catalytic Additives on Transformation of Highly Viscous Heavy Oil

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Received March 25, 2015

Abstract—The influence of the rock-forming additives kaolin and alumina in the presence of nickel compounds on the thermal catalytic conversion of heavy oil at a temperature of 360°C in a reducing atmosphere at different pressures in the system has been revealed. The effect of poly- α -olefins as a hydrogen donor has been examined. It has been found that there are predominant degradation reactions of the resinous components, aliphatic substituents in asphaltenes, and branched aliphatic structures accompanied by redistribution of *n*-alkanes toward homologues with a lower molecular weight, resulting in reduction in the viscosity of heavy oil. Conducting the process in the presence of Al₂O₃, Ni, and poly- α -olefins at a pressure of 8 MPa increases the quantity of light fractions of the oil and facilitates the degradation of asphaltenes. A decrease of pressure in the experiment on the oil with kaolin in a reducing atmosphere leads to a decrease in aromaticity of the final product and an increase in the yield of lube oil hydrocarbon and low-boiling fractions.

Keywords: heavy oil, carbonate additive, kaolin, aquathermolysis, bulk composition, molecular weight distribution of *n*-alkanes

DOI: 10.1134/S0965544116010059

There is increasing worldwide interest in the development of alternative types of reserves of hydrocarbon resources, such as gas hydrates, shale oil and gas, heavy oil, and natural bitumen. The world reserves of natural bitumen are estimated at 260 billion tons by the United Nations. Natural bitumen and heavy oils are characterized by complex mode of occurrence and unique composition and properties. Their development is impossible without the creation of innovative producing and refining technologies capable of converting unconventional hydrocarbon resources into demanded petrochemical feedstock, which requires, in turn, the development of new basic scientific knowledge. So scientific investigations and research and development works aimed at involving the hydrocarbon resources of the new type are in progress and advanced, although capital-intensive technologies of their production and cost-effective processing are developed around the world [1].

The research in leading scientific centers arch have focused since recently on the development of techniques and processes of reservoir management leading to partial upgrading of heavy hydrocarbon feedstock on-site [2]. Russian research works devoted to the study and identification of trends in the behavior of the chemical composition of hydrocarbon fluids, depend-

ing on the mineral composition and the presence of trace elements in source rock under the influence of natural and anthropogenic factors are of particular interest. Transformations in heavy oils under the conditions of steam injection into carbonate reservoirs at temperatures up to 350°C and pressures up to 7.1 MPa are accompanied by an increase in amount of resin-asphaltene compounds (RAC), aromatic structures, and oxygen-containing functional groups in the oil composition; the formation of insoluble carbonization products; and an increase in the concentration of higher *n*-alkanes in lube oils [3].

Thermal degradation of macromolecular petroleum compounds in the temperature range of 325–425°C in the presence of quartz promotes the formation of substances with a lower molecular weight; macromolecular products are preferentially formed with calcite; and the amount of low-molecular-weight compounds, in particular, aromatics, and saturated hydrocarbons increases in the presence of montmorillonite and quartz [4]. In contrast, hydrothermal treatment in a flow system in a reducing hydrogen atmosphere at temperatures up to 360°C leads to a decrease in the amount of soluble and insoluble organic matter (OM) in the rocks and the oil recovered has an increased proportion of lighter hydrocarbons, reduced

total sulfur content, and decreased amounts of vanadyl porphyrin complexes and trace elements [5]. The sorptive and catalytic effect of rock-forming minerals and the presence of ambient air with the aqueous phase may facilitate the degradation of high-molecular-weight components of the heavy oil and, thus, increase the oil recovery factor of pay formations [3, 5].

The purpose of this work was to reveal the trends of change in the composition of high-viscosity heavy oil under the influence of thermocatalytic factors in the presence of rock-forming compounds.

EXPERIMENTAL

The object of study was a sample of heavy oil produced by the steam-assisted gravity drainage technology from the Ashal'chinskoye oilfield of Tatarstan [6]. The productive sediments are Devonian and Lower Carboniferous terrigenous reservoirs and Devonian and Middle Carboniferous carbonate rocks [7].

The thermocatalytic upgrading of the oil was studied in a laboratory batch reactor (autoclave) under isothermal conditions at high temperatures and pressures (Table 1); the experimental run time was 2.5 h. After the run, the final product was withdrawn, free water separated after settling was removed, a demulsifier was dosed (0.001%) with a microsyringe, and the product was agitated in a shaker for 10–12 min and then placed in a thermal cabinet at 80°C for 2 h; after that, settled water was removed again.

As compounds making the source rock, we selected carbonate (marble), consisting of calcite and dolomite, and kaolin clay. Water was taken as an effective medium for the uniform distribution of heat throughout the reaction mixture that prevents carbonization reactions, and an acidic environment was created with ethanoic acid. Additives, preliminarily subjected to dispersing, were introduced into the reaction mixture through the aqueous phase. The dispersion of the additives to increase their specific surface area was performed using an ultrasonic device with a frequency of 22 kHz and an energy density of 5 W/cm². The particle size of Al₂O₃ was 4.3–7.18 × 10⁻⁷ m (87.5%) and 0.59–0.8 × 10⁻⁷ m (12.5%), and that of kaolin was 2.94–6.38 × 10⁻⁷ m (69.8%) and 0.53–0.85 × 10⁻⁷ m (30.2%). The choice of suspended metal-containing additives was determined by the following factors: Ni and Cu salts can exhibit both hydrogenating and dehydrogenating activity; Al₂O₃ has significant catalytic activity for cracking hydrocarbons; methyl isobutyl ketone-stabilized nickel(II) oxide particles of a size up to 50 × 10⁻⁹ m can exhibit oxidizing activity in an aqueous medium; poly- α -olefins (PAO) are characterized by a high hydrogen content and, thus, have been considered a hydrogen source [8]. The advantage of nanoparticles is their accessibility for organic molecules of any shape and size, which is especially impor-

tant in the processing of heavy hydrocarbon feedstocks [9, 10].

To study the bulk composition of the liquid products, asphaltenes were preliminarily precipitated with a 40-fold excess of petroleum ether (boiling point 40–70°C); then, the group of saturated hydrocarbons and two groups of resins, benzene extractable (BR) and alcohol–benzene extractable (ABR) resins, were isolated by liquid adsorption chromatography.

The molecular weight distribution (MWD) of *n*-alkanes was determined with a TurboMass Gold quadrupole mass spectrometer GC/MS system (PerkinElmer). A fused-silica capillary column of a 30 m length and a 0.32 mm inner diameter coated with the stationary phase SE-52 was used; helium was the carrier gas. Analyses were carried out in the linear temperature programming mode from 40 to 280°C at a heating rate of 4°C/min. Mass spectrometric detection was performed in the selective ion monitoring mode to record mass fragmentograms. The software NIST was used for data processing, and identification of *n*-alkanes was performed with reference to published data [3, 11, 12].

The structural-group composition of transformed oils was studied using IR spectroscopy [8]. The IR spectra displayed characteristic intense absorption bands due to aliphatic structures at 1380 and 1465 cm⁻¹, paraffinic structures at 720 cm⁻¹, aromatics at 1600 cm⁻¹, sulfoxide groups at 1030 cm⁻¹, and ester carboxyl groups at 1740 cm⁻¹.

Rheological studies of oil samples were performed in the cone–plate geometry at the shear rate ranging from 3 to 1312 s⁻¹ and the temperature ranging from 10 to 80°C on a Reotest 2 rotary viscometer according to GOST 25276-82. Dynamic viscosity was determined according to GOST 33-2000 (ISO 3104-94).

The elemental composition of asphaltenes was determined by combustion in a semi-automated C, H, N analyzer.

RESULTS AND DISCUSSION

The presence of the carbonate additive and Al₂O₃ in a finely divided state in the oil under the temperature and pressure conditions of the experiment (run 1, Table 1) leads to a decrease in the amount of benzene resins (BR) by 17% as a result of initiation of radical chain degradation reactions and an increase in the proportion of ABR, a change that may indicate the occurrence of cracking reactions, since the viscosity of the sample was significantly reduced from 658 to 130 mPa s. The high viscosity of the heavy oil was due to the presence of native asphaltenes having the “loose” structure, and the decrease in viscosity in the experiments was caused by the thermally induced degradation of their side aliphatic structures to form more compact secondary asphaltenes with a lower molecular weight [13]. An increase in the proportion of ABR and a simultaneous decrease in the proportion of

Table 1. Characteristics of products of thermocatalytic conversion of heavy oil

| Composition of reaction mixture | Density at 20°C, kg/cm ³ | Viscosity at 40°C, mPa s | Bulk composition, wt %* | | | | |
|--|-------------------------------------|--------------------------|-------------------------|------|------|----------|-------------|
| | | | HC | BR | ABR | Σ resins | asphaltenes |
| Original oil (contr.) | 0.9500 | 658 | 57.9 | 19.8 | 15.8 | 35.6 | 6.5 |
| Product of run 1 (<i>T</i> 375°C, <i>P</i> 13.5 MPa, water : oil = 1 : 2, carbonate 2.4%, Al ₂ O ₃ 2.3%) | | | | | | | |
| No. 1, oil, water, carbonate, Al ₂ O ₃ | 0.9641 | 130 | 59.9 | 16.3 | 16.9 | 33.2 | 6.9 |
| Product of run 3 (<i>T</i> 350°C, <i>P</i> 7.8 MPa, water : oil = 1 : 2, kaolin 2.4%, NiSO ₄ : CuSO ₄ (3 : 1) 2.4%) | | | | | | | |
| No. 3, oil, water, kaolin, NiSO ₄ , CuSO ₄ | 0.9499 | 182 | 61.4 | 17.4 | 15.1 | 32.5 | 6.1 |
| Product of run 5 (<i>T</i> 350°C, <i>P</i> 7.8 MPa, water : oil = 1 : 2, Al ₂ O ₃ 2.4%, Ni (PAO) 10.1%) | | | | | | | |
| No. 5, oil, water, Al ₂ O ₃ , Ni (PAO) | 0.9312 | 131 | 56.7 | 19.9 | 18.8 | 38.7 | 4.6 |
| Product of run 7 (<i>T</i> 360°C, <i>P</i> 1.2 MPa, water : oil = 1 : 4, kaolin 7%, C ₂ H ₄ O ₂ 14%) | | | | | | | |
| No. 7, oil, water, kaolin, C ₂ H ₄ O ₂ | 1.0304 | 650 | 62.2 | 19.3 | 12.6 | 31.9 | 5.9 |

* Bulk composition of topped samples of heavy oil boiling above 200°C.

asphaltenes may be indicative of transformation (conversion or redistribution) of part of the asphaltene structures into ABR.

The introduction of Ni and poly- α -olefins into the reaction mixture with Al₂O₃ in the nanosized state in run 5 leads to a noticeable reduction in the concentration of asphaltenes (by 29%) in the transformed oil and an increase in the ABR content. It is likely that the additives Ni and poly- α -olefins have a considerable effect on the processes of thermal degradation of highly condensed aromatic structures in this case, as well as the reduction in pressure to 7.8 MPa versus 13.5 MPa the first run. In the case of thermal treatment of the heavy oil in the presence of kaolin clay and Ni and Cu salts at 350°C and a pressure of 7.8 MPa (run 3, Table 1), the amount of BR in the oil decreases and the lube oil content increases by 6%. The treatment with kaolin clay in a reducing medium (run 7, Table 1) leads to a decrease in the amount of alcohol-benzene resins and an increase in the lube oil content by 7.4%.

Comparison of the results of component analysis of the heavy oil and the products of its thermal catalytic processing shows preferential conversion of resins to form lighter hydrocarbons of the lube oil group. Since neither the amount of asphaltenes nor the proportion of carbonaceous substances in the samples of the transformed oil increased, it follows that both the temperature conditions and the oil : water ratio in the experiments were chosen properly. At aquathermolysis temperatures of the heavy oil below 375°C, the reactions of resin compaction into asphaltenes are enhanced. Aquathermolysis under supercritical conditions initiates the cracking reactions of the resinous components, which lead to a decrease in the number and length of aliphatic substituents, degradation of naphthenic moieties, and a dramatic reduction in the size of asphaltenes [3].

The composition of the transformed oil after the first run with the carbonate additive and Al₂O₃ shows an increase in the yield of the gasoline fraction from 9.8 to 15%, an insignificant decrease in the amount of the 200–350°C fraction (Fig. 1), and displacement of the MWD maximum of *n*-alkanes to homologues with a lower molecular weight (Fig. 2).

The gasoline fraction of both the starting oil and its transformation product is dominated by cyclopentane and isoprenoid hydrocarbons. The yield of light fractions markedly increases to 39% in the oil transformed at 350°C and a pressure of 7.8 MPa in the presence of nanosized Al₂O₃ and Ni particles in poly- α -olefins; the olefins are apparently involved in cracking reactions to form predominantly C₂₇–C₂₉ *n*-alkanes, and the yield of the higher C₃₂–C₃₉ *n*-alkanes decreases. In the oil transformed in the reducing environment in the seventh run with kaolin in the reaction mixture, the amount of the gasoline and diesel fractions increases to 42%; in addition, the proportion of higher homologues having the number of *n*-alkane carbon atoms greater than 21 markedly increases, indicating a higher content of solid paraffins in the sample. In general, the final products of the experiments differ from those of the initial crude oil by a more uniform MWD of *n*-alkanes, a greater yield of the lower C₁₄–C₁₈ homologues, and minor manifestation of the bimodality (which is distinct in the initial sample) due to the detachment of aliphatic chains from asphaltenes and the cracking of isoprenoid structures.

Table 2 shows the elemental composition of the initial oil and the final products of the experiments. The thermobaric experimental conditions result in a slight decrease in the amount of organic sulfur compounds in the final products; the least stable C–S bonds undergo degradation.

The aquathermolysis of the heavy oil in the presence of the carbonate additive and kaolin leads to aro-

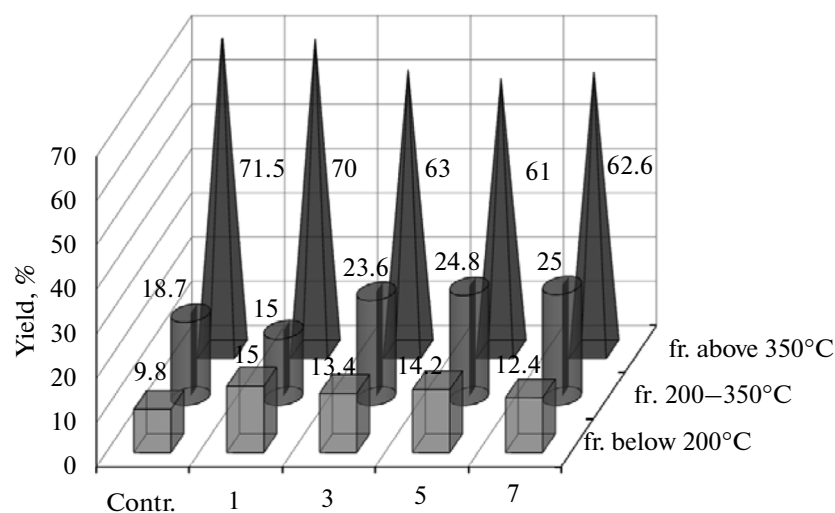


Fig. 1. Fractional composition of transformed oil.

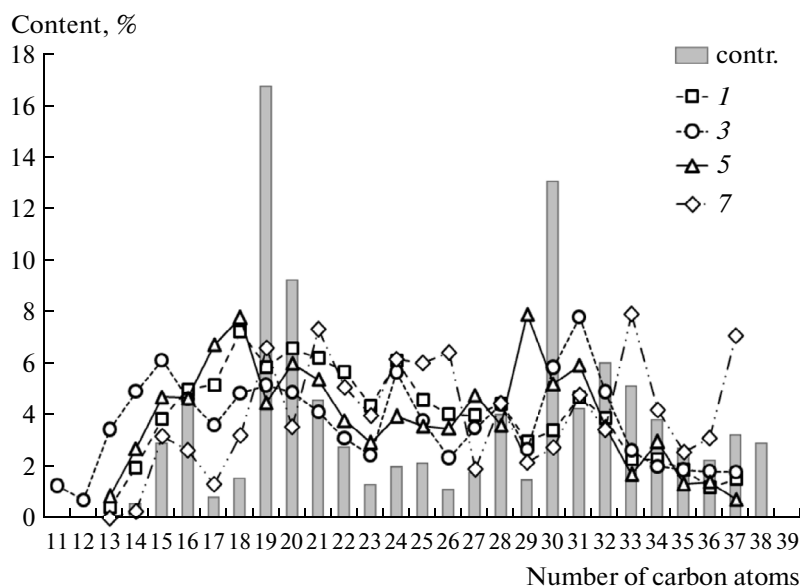


Fig. 2. Molecular weight distribution of *n*-alkanes in the products of transformed oil.

matization of the oil, a change that is confirmed by published data [3]. In contrast, the reducing environment and the presence of a hydrogen source in the form of poly- α -olefins in the fifth (350°C, 7.8 MPa) and seventh (360°C, 1.2 MPa) runs reduces the degree of aromaticity of the transformed oils, as evidenced by higher H/C values. The high nitrogen content is due to greater stability of nitrogen in fused polyaromatic structures.

The results of the study of aquathermolysis of the heavy oil with the carbonate additive and kaolin at temperatures above 350°C show the prevalent occurrence of cracking reactions of the resinous components, aliphatic substituents on asphaltenes, and

branched structures, which result in a decrease in viscosity of the transformed oil and the redistribution of *n*-alkanes in favor of lower homologues. The process in the presence of Al₂O₃, Ni, and poly- α -olefins results in an increase in the amount of light fractions of the oil and the degradation of asphaltenes leading to the accumulation of alcohol–benzene resins. Lowering the pressure in the experiment on the oil with kaolin in a reducing atmosphere decreases the aromaticity of the final product and increased the yield of lube oil hydrocarbons and low-boiling fractions.

As shown by the data in Fig. 3, the oil transformed in the 7th run in the presence of both kaolin and the carboxylic acid has a higher viscosity, which is presum-

Table 2. Elemental composition of transformed oils

| Sample | S | N | C | H | H/C |
|---|-----|-----|------|------|-------|
| Oil (contr.) | 2.8 | 0.4 | 80.6 | 12.9 | 0.160 |
| No. 1, oil, water, carbonate, Al ₂ O ₃ | 2.5 | 2.6 | 79.9 | 12.1 | 0.15 |
| No. 3, oil, water, kaolin, NiSO ₄ , CuSO ₄ | 2.3 | 2.1 | 79.6 | 12.2 | 0.153 |
| No. 5, oil, water, Al ₂ O ₃ , Ni(PAO) | 1.5 | 1.3 | 81.2 | 13.2 | 0.163 |
| No. 7, oil, water, kaolin, C ₂ H ₄ O ₂ | 2.5 | 0.7 | 81.7 | 13.6 | 0.167 |

Table 3. Elemental composition of transformed oils

| Run no., composition of initial mixture | Optical density D at absorption band maximum, λ cm ⁻¹ | | | | | | Spectral factors* | | | |
|---|--|-------|-------|-------|-------|-------|-------------------|----------------|----------------|----------------|
| | 1740 | 1600 | 1465 | 1380 | 1030 | 720 | C ₁ | C ₃ | C ₄ | C ₅ |
| Control | 0.022 | 0.214 | 1.015 | 1.018 | 0.133 | 0.188 | 1.14 | 1.00 | 5.62 | 0.13 |
| No. 1, oil, water, carbonate, Al ₂ O ₃ | 0.024 | 0.238 | 1.300 | 0.724 | 0.055 | 0.191 | 1.24 | 0.56 | 3.84 | 0.04 |
| No. 3, oil, water, kaolin, NiCu | 0.026 | 0.227 | 1.874 | 0.884 | 0.175 | 0.210 | 1.08 | 0.47 | 4.8 | 0.09 |
| No. 5, oil, water, Al ₂ O ₃ , Ni(PAO) | 0.010 | 0.061 | 0.493 | 0.267 | 0.033 | 0.038 | 1.59 | 0.54 | 4.97 | 0.07 |
| 7, oil, water, kaolin, C ₂ H ₄ O ₂ | 0.034 | 0.186 | 1.456 | 0.785 | 0.134 | 0.152 | 1.22 | 0.54 | 5.03 | 0.09 |

* C₁ = D_{1600}/D_{720} (aromaticity); C₃ = D_{1380}/D_{1465} (branching); C₄ = $(D_{720} + D_{1380})/D_{1600}$ (paraffinicity); C₅ = D_{1030}/D_{1465} (sulfurization).

ably due to the kaolin contained in the final product. Resulting oil samples 1, 3, and 5 have a lower viscosity than the initial oil and are characterized by less steeper viscosity–temperature curve, which, in turn, may be associated with quantitative redistribution of n -alkanes in these samples (Fig. 2) towards the buildup of the lower C₁₁–C₁₈ homologues. The liquid products of the experiments with Al₂O₃ (runs 1 and 5) contain a negligible amount of C₃₀–C₃₈ n -alkanes. The inset in Fig. 3 shows differences between the rheological curves of the samples in the temperature range of 50 to 90°C.

The results of the spectroscopic study of the aquathermolysis of heavy oil (Table 2) shows that the final products of the process are characterized by low values of branching, which are apparently due to reactions involving C–C bond scission at tertiary carbons in isoprenoid structures and the detachment of peripheral substituents in polycondensed aromatic structures. The paraffinicity index changes in a similar manner, also suggesting the occurrence of cracking reactions of higher paraffin hydrocarbons and the buildup of their homologues in the final products. The sulfurization index in all the products is lower than that of the starting oil, indicating the decomposition of sulfur compounds to form hydrogen sulfide. During the experiments, the formation of gaseous hydrocarbons and hydrogen sulfide was observed.

On the basis of comparative analysis of the spectral parameters of the heavy oil before and after the experiments, the following should be noted: at the temperature and pressure of the first run in the presence of the carbonate additive and Al₂O₃, degradation reactions and the abstraction of peripheral paraffin substituents proceeded to a more complete extent; moreover, the product sample had the lowest sulfur content and paraffinicity; the products of runs 3 and 5 are relatively similar in spectral parameters; but the final product of the seventh run is characterized by the smallest changes in spectral factors of aromaticity, paraffinicity, and sulfurization compared with the original oil.

Thus, it has been found that the steam conversion of heavy oil in the presence of rock-forming mineral additives and Ni and Cu salts at temperatures and pressures up to 375°C and 13 MPa, respectively, reduces the density and viscosity of the resulting oil and increases the concentration of saturated hydrocarbons and the yield of light ends. The distribution of n -alkanes is altered towards the formation of lower homologues. The chemistry of the process involves the radical chain mechanism and is described by cracking reactions and compaction of the intermolecular structure of asphaltenes.

The results of the study can turn useful for the designing of innovative technologies of development of heavy oil and natural bitumen deposits.

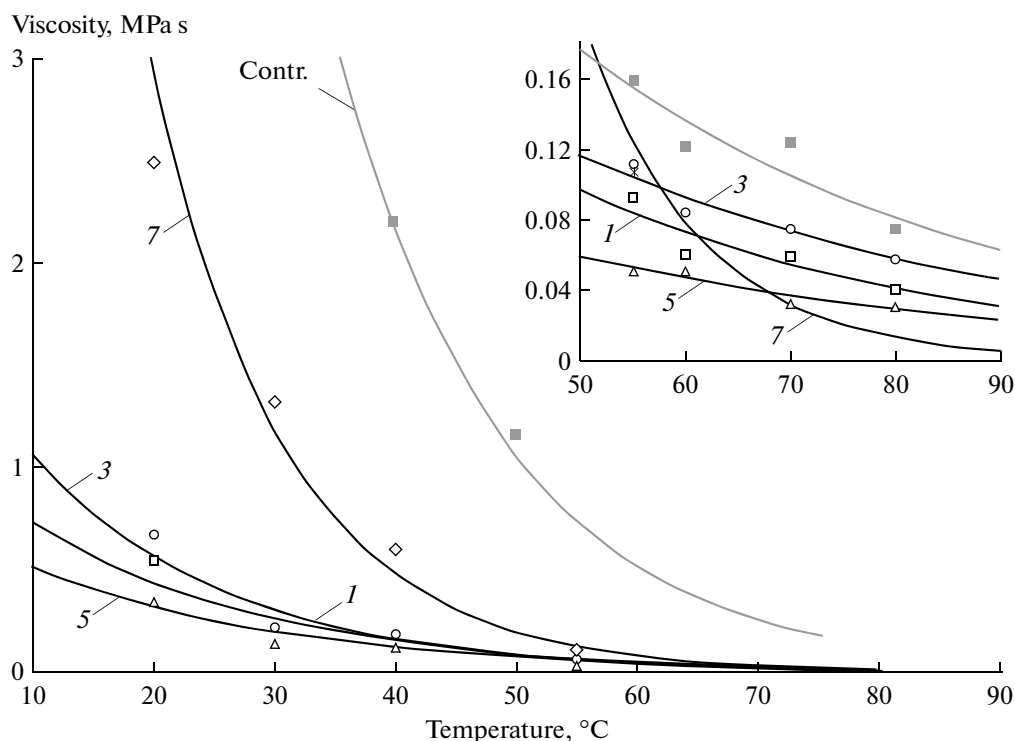


Fig. 3. Temperature dependence of the dynamic viscosity of the original and the transformed oil. Contr. refers to the dynamic viscosity of the original oil, and curves 1, 3, 5, and 7 refer to the dynamic viscosity of the oil transformed in runs 1, 3, 5, and 7, respectively.

ACKNOWLEDGMENTS

This work was supported by the President of the Russian Federation, grant no. MK-2054.2014.5, and the under the program of state support of the Kazan Federal University to improve its competitiveness among world leading research and education centers.

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Translated by S. Zatonsky