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Anomalous Viscosity of High-Molecular Petroleum Fractions in Process of Relaxation after High-Intensity Ultrasonic Treatment

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Abstract

Background/Objectives: Lower output of light oil and gradual depletion of its resources result in stronger interest in developing heavy oil deposits. However, its extraction is complicated because of its high viscosity. **Methods:** Principal methods of reducing oil viscosity imply preheating the oil-bearing bed and applying solvent agents. However, those methods are expensive and environmentally insecure. Another method is represented by high-intensity ultrasonic treatment. Its application helps reduce expenses and is environmentally safe. Therefore, there is an interest in the petroleum extraction practices that apply ultrasound. Such methods are developed in China, Iran, Russia, the USA, Western Europe and in other countries. **Findings:** The authors have investigated the effects produced by different kinds of ultrasonic treatment on kinematic viscosity of such oil products as black oil grade M-100, applying the ultrasound of different power and duration. The samples of black oil were subjected to direct effects of high-intensity treatment and the kinetic viscosity was measured before and after the treatment. Within 10 days, in the process of relaxation, the changes in viscosity of the treated samples were observed. The dependencies of viscosity on the duration of the fixed power ultrasound treatment have been discovered, the nonlinear and non-monotone nature of those dependencies have been established. Anomalous non-monotone nature of viscosity change in black oil grade M-100 has been observed. Under some modes of treatment, periods of viscosity lowering were observed. These anomalies are likely to be caused by the clots that were formed of the most viscous fractions of the product and that left the fractions with lower viscosity beyond, thus explaining the lower total viscosity in the process of relaxation. **Applications/Improvements:** The results can be used for selecting the regimes of ultrasonic treatment for the purposes of developing heavy oil production equipment and for improving petroleum and oil products handling operations.

Keywords: High-Molecular Petroleum Fractions, High-Intensity Ultrasonic Treatment, Relaxation, Viscosity

1. Introduction

Today in Russia 55% of the proven oil reserves consist of heavy oil but its share in overall oil production makes just 15%. This is explained by the difficulties associated with producing, transporting and processing heavy grades of oil that are preeminently caused by their high viscosity. Different methods are applied to reduce the viscosity of the heavy oil including such techniques as: Hot water flooding, cyclic steam stimulation, steam oil drive, Steam Assisted Gravity Drainage (SAGD), introducing solvent agents, fire flooding etc[1,2]. The methods associated with steam or hot water are highly energy-consuming which increases the prime-cost of production and reduces the general competitiveness of the heavy grades of oil. The methods associated with solvent agents and other chemicals that could facilitate the extraction process, apart from being expensive, are also considerably detrimental from the perspective of environmental protection. The above mentioned circumstances make producers look for less energy-intensive and more environmentally friendly methods for producing high-viscosity heavy

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oil. One of the few effects known to reduce the viscosity of the heavy grades of oil without any serious damages to the environment is represented by high-intensity ultrasonic treatment. This technology is widely applied for processing the face and bottom-hole areas of the oil well to clean the gun perforation zones off colmatation and paraffin plugs that hamper extraction. It is also a well-known fact[3,4] that intensive ultrasound treatment can change mechanical properties of high-viscosity liquids including different kinds of petroleum, biological liquids and liquid hydrocarbons; particularly, such an effect on the compounds of high-molecular hydrocarbons results in their temporally lower viscosity[5–8]. Thus, it is obvious that wider application of ultrasound in developing heavy oil deposits makes it possible to cut expenses for its production and reduce environmental footprint on the deposit fields. Today different methods of ultrasonic treatment applied in the process of extracting and handling heavy grades of oil give way to the most widely applied methods of preheating and solvent treatment; however, the evident advantages that are expected to be obtained by applying ultrasound in this area make researchers and manufacturers in different countries of the world embark on developing the new improved methods of ultrasound treatment for processing heavy oil and high-viscous oil products. In particular, sono-chemical approaches aimed at improving the oil recovery of the field have been discussed in a special study[9] that also presents correlations occurring in the process of destruction of the intermolecular bonds and shows the graph describing oil viscosity relaxation upon ultrasonic treatment. Another work[10] studies kinetics of bitumen water extraction obtained from bituminous sand and that of the crude oil or black oil obtained from the model contaminated soils and treated with ultrasound; it also investigates the effects produced by temperature, powerful ultrasound and concentration of the admixed alkali agents on the oil production intensity. Scientists from Iran[11] have paid their attention to studying the effects produced by temperature, solvent concentration and ultrasonic radiation on reducing viscosity of the black oil; most peculiar about this investigation was the fact that for the purpose of reducing viscosity of black oil the authors used ultrasound radiation with low frequency of 24 kHz. It has been demonstrated that, under such treatment, the viscosity used to drop more than 1.5 times. Yet another study described the state of the investigations and the trends in developing ultrasonic oil production methods in China. In[12] this work represents the review of the developments and the trends in applying ultrasound for improving the oil recovery index. Ultrasound assisted oil production practices in China and in other countries have been compared; latest achievements and successful practical applications of the ultrasound oil production in China have been generalized. New method of ultrasound-based method for increasing oil production output that assumes continuous ultrasound treatment in the course of extraction has been described in a separate comprehensive study[13] while another research work[14] provides another review of the existing modern technologies including the patented methods of processing the extracted heavy oils. One more study[15] provides theoretical and experimental investigations on dehydration and desalination of petroleum applying static ultrasonic waves in the newly designed reactor, analyzing the effects produced by the principal parameters, including the parameters of ultrasonic radiation. Based on the experimental data, two kinds of evaluations have been introduced to obtain the correlations existing between desalination, dehydration and the required input energy. Other works[16–21] also provide important data on performance of the oil products after ultrasonic treatment. This study presents the results of investigating the dependency of kinematic viscosity of heavy oil fractions on highly-intensive ultrasonic treatment of varying duration.

2. Method

Insofar as the objective of this study was to investigate the effect produced by ultrasound on the viscosity of the oil products which could be of practical interest, the subjects of the investigation could be represented either by the most viscous petroleum products, on the one hand, or by the most widely spread ones. Therefore, the primary distillation product, black oil grade M-100 that is one of the most widely applied products of this type in Russia and CIS was selected as the object of this study. While choosing the character of the ultrasound treatment the authors of this study faced certain problems. In most application areas, the high-intensity ultrasound is applied continuously and at one constant frequency. This is explained by high degree of inconsistency between the acoustic resistance of the active materials used for manufacturing the ultrasonic radiators and that of the majority of liquids used as an acoustic load, for instance, water, oil, biological liquids, etc. Given the large difference in the acoustic resistance values, a considerable reflection of the acoustic waves is observed at the border dividing the radiator and water; therefore, the high-quality resonant radiators operating in the narrow frequency range prove to be most efficient for the purpose. Such transducers are, particularly, represented by Langevin transducers. Radio impulse or mono impulse treatment is used less often and then the sources are usually represented by the wide band pass radiators that feature complicated structure and short service life. Medical science is an exception to this rule; here the high-intensity impulse and radio impulse ultrasound has been widely applied as therapeutic and surgical treatment employing different types of ultrasonic transducers including those that use piezocomposite materials acoustically aligned with the load media[22–24]. Besides, high-intensity impulse ultrasound is applied in the systems for removing air from liquids, in the systems for removing lime scale from the walls of the pipes and boilers and in some other technical applications. Consequently, studying the effects of the continuous uninterrupted ultrasonic treatment seemed to bring about fast and plausible success, however, a number of data[25,26] indicated that the effect produced by powerful ultrasound on viscous media including high-viscosity liquid hydrocarbons could prove to be more efficient in terms of destructing the intermolecular bonds that basically cause their high viscosity. Thereat, to make a justified selection of the impulse method of ultrasonic treatment, large number of parameters had to be compared including the amplitude of ultrasonic impulse, pulse ratio, width of the band pass, duration, etc. At the initial stage of the investigation, this was impossible; therefore, the authors started with continuous uninterrupted ultrasonic treatment. The source of the ultrasound was represented by Langevin transducer with operating frequency of 37 kHz and with radiation surface diameter of 40 mm. The body of this transducer was made of duralumin grade D16-T in the shape of frustum of a cone. Diameter of the narrow end of the cone at the active elements was 36 mm, diameter of the external part made 40 mm, the height of the cone was 18 mm, the rear part of the radiator represented a cylinder made of steel grade 45, 36 mm in diameter and 15 mm thick; active section of the transducer consisted of two rings made of piezoelectric material grade PCR-78, each ring having the inner diameter of 20 mm, and the outer diameter of 36 mm, 4 mm high. The rings were placed within the structure of the radiator in such a way that their polarization vectors opposed one another. All structure was fixed with bolt M10 made of steel grade 45. The source of the uninterrupted signal with the required power was represented by the complex unit that included signal generator Tektronix AFG 3022 B and amplifier PA 400-5 manufactured by Precision Acoustics LTD. The signal from the generator was fed to the amplifier, then from the amplifier through the aligning transformer to the electrodes of the radiator. The measurements of kinematic viscosity of the oil product were taken with viscometer VZ-246 featuring operating chamber of 100 mm^3 and replaceable flow orifices with diameters 2, 4 and 6 mm. It was calibrated under temperatures of 22, 25, 40, 50 and 80°C using high purity glycerin as benchmark material. Relative measurement error during calibration amounted to 2.7% with flow orifice diameter of 2 mm; 3% with viscometer flow orifice diameter of 4 mm and 3.5% with orifice diameter of 6 mm. Investigations were carried out according to the method as follows:

- A sample was formed as 200 cm^3 of the liquid under investigation in the glass of 80 mm depth; the temperature of the sample was measured, 100 cm^3 of the above mentioned volume was poured onto viscometer and then the initial kinematic viscosity of the liquid was established based on the obtained data;
- A sample of 200 cm^3 of liquid was placed in such a manner that the radiating surface of the transducer was fully immersed into the liquid by the depth of 1 mm, the transducer was fed with an uninterrupted signal of 30 W;
- Upon ultrasound treatment, the temperature and kinematic viscosity of the sample were measured again;
- The obtained results were analyzed.
- Steps 1-4 were repeated for the durations of the uninterrupted signal of 60, 120, 300, 450, 600, 750, 900 and 1200 seconds.
- After the periods equal to 1, 2, 3, 4, 5, 48, 96, 144 and 240 hours after the treatment the temperature and the kinematic viscosity of the samples were measured in order to trace the dynamics of the relaxation processes occurring in the liquid that underwent ultrasonic treatment.

3. Results

Dependencies occurring between kinematic viscosity of black oil M-100 (reduced to 25°C) after ultrasonic treatment with power 30 W and frequency of 36.6 kHz with processing durations of 60, 150, 450, 600 and 1200 s and the time after ultrasonic treatment are shown in Figures 1 and 2. The samples from two batches of black oil were studied. The samples from the first batch at 25°C possessed initial viscosity values of 15500-16700 mm^2/s, viscosity of the samples from the second batch made 15400-17000 mm^2/s. Average initial kinematic viscosity at 25°C amounted to 16 200 mm^2/s. Figure 1 shows the dependency limited by 240 h that passed from the moment of ultrasonic treatment. Each point on the graph is a result of averaging of 4 to 12 measurements. Relative error of measurements was found to be 7 to 40 % for the durations after treatment of 0 to 6 h, and 9 to 27 % for durations of 48 to 240 h. The behavior of the viscosity within short durations after treatment (not longer than 5 h) is shown in more detail in Figure 2. In this area, the monotone growth of kinematic viscosity is observed depending on the time that has passed after the treatment for all samples irrespective of the duration of their treatment. Directly after the treatment, inverse dependence of kinematic viscosity on the duration of ultrasonic treatment is observed; however, in the process of relaxation, viscosity of the samples under different modes of treatment grows with different velocity and, in a number of cases, the viscosity of the initially less viscous samples is higher that the viscosity of those initially more viscous.

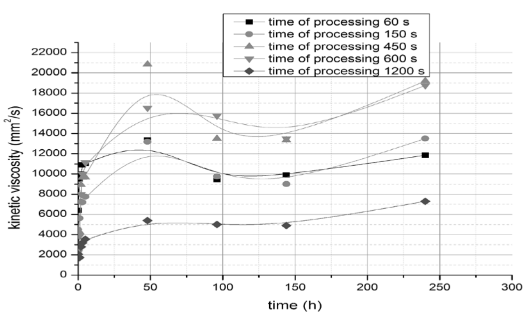

Figure 1. Time dependence of kinematic viscosity of black oil M-100 (reduced to 25°C) after ultrasonic treatment within the period of 0-240 hours.

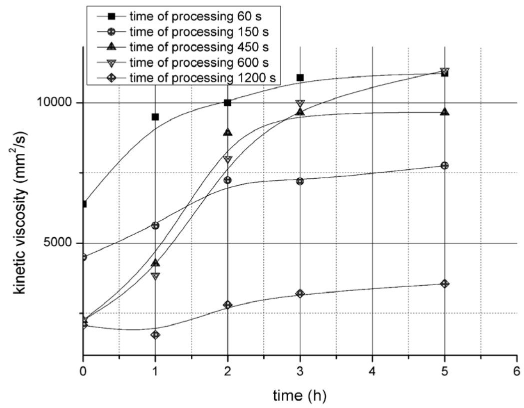

Figure 2. Time dependence of kinematic viscosity of black oil M-100 (reduced to 25°C) after ultrasonic treatment within the period of 0-5 hours.

As a result of ultrasonic treatment, the samples were heated considerably. In particular, under the treatment lasting for 1200 s the samples used to heat up to the temperatures of 75-78°C. Given the fact that the temperature of black oil M-100 flash-point is 110°C and that it is reasonable to assume that this treatment could decrease the flash-point, the duration of ultrasonic treatment had to be limited by 1200 s. Kinematic viscosity of black oil M-100 depends on temperature considerably. After ultrasonic treatment the authors of this study obtained samples with different temperatures depending on the duration of the ultrasonic treatment; the process of cooling down to the temperature of the environment took several hours; thereat, the relaxation processes that occurred simultaneously resulted in considerable changes in the viscosity of the samples. The efforts to expedite the process of cooling the samples would inevitably result in additional factors affecting the results of the investigation. To make it possible to compare kinematic viscosity values of the samples with different temperatures, their viscosity values were reduced to conditional viscosity that corresponds to the viscosity under temperature of 25°C. Using conditional viscosity was relevant for the first 5 h after the treatment, insofar as after this period the samples used to cool down to the temperature of the laboratory where it was maintained at the level of 24-25°C during the investigation; consequently, upon 5 h after the treatment, the reduced kinematic viscosity was insignificantly different from the actually measured one.

3. Discussion

As a result of the interactions, kinematic viscosity of the black oil decreased by several times. As a rule, black oil relaxation to the condition that is close to the initial condition took longer than 10 days. The anomalous non-monotone nature of the change in the viscosity of the substance should be noted. Within the period of 50-150 h the decrease in viscosity was observed, then viscosity started increasing again. Obviously, this is explained by the complex processes of reconstructing the intermolecular bonds in the course of relaxation. In the process of taking viscometer measurements, the formation of clot was observed. Presumably, due to the concentration of the most viscous fractions of the liquid in the clot, the substance that was left beyond the clot became less viscous, thus resulting in temporal drop of the total kinematic viscosity of black oil M-100; then, as the intermolecular bonds were reconstructed in the course of relaxation, the average size of the clot grew resulting in the renewed increase in viscosity. This assumption has to be confirmed later in the course of the investigations that should follow. Under some certain modes of treatment, in the course of relaxation, the initial viscosity values proved to be less than those obtained in the course of ultrasonic treatment followed by relaxation. This can be explained by the effect of rejuvenation occurring in intermolecular bonds that were previously destroyed by ultrasonic treatment and then were reconstructed in the course of relaxation.

Comparing the obtained results with the data submitted by other authors in the research studies mentioned above, it is possible to maintain that the described general trends in changing viscosity of oil and oil products of different kinds after ultrasonic treatment do coincide. Indeed, all results of the studied investigations show that under high-intensity ultrasonic treatment of the heavy grades of oil and oil products with high viscosity, the viscosity of those substances decreases; the kinematic viscosity illustrated in some studies as well as the dynamic viscosity illustrated in other studies become lower that the initial viscosity immediately after the treatment. In fact, in the process of relaxation that takes several days, the viscosity of the oil products that underwent ultrasonic treatment is rehabilitated partially or in full. However, there are some discrepancies. First and foremost, it seems strange that practically none of the studies mention that oil and oil products are heated during the process of ultrasonic treatment. Meanwhile, the temperature is one of the most important factors that affect viscosity of these substances and it is hardly possible to neglect this effect without compromising the results of the investigations considerably. The second important difference of this study is the fact that the authors discovered the anomalous behavior of viscosity of the black oil in the course of relaxation. The periods were discovered when the viscosity of the black oil not only dropped, but also increased in the course of relaxation. This may be explained by the fact that the objects of the investigations were different. The study that described almost similar parameters[11] was dedicated to investigating the effect produced by ultrasonic treatment on black oil. However, the initial kinematic viscosity of black oil at 20°C amounted, in that study, to 4940 mm^2/s that testifies to the fact that the object of the investigation was represented by the black oil similar to Russian navy oils that are obtained by admixing diesel fuel to black oil M-100 in order to decrease viscosity, i.e., even in this case, the objects of the investigations were considerably different and so were the results.

It should be noted that black oil is one of the oil products that are mostly inconstant in their composition and the real chemical composition of different batches of black oil of one and the same grade can be significantly different; consequently, their physical and mechanical properties will differ as well. However, the scale of the effect of decreasing the viscosity of black oil as a result of ultrasonic treatment followed by relaxation that was discovered in the course of this study makes it possible to assume that this effect will show itself to one degree or another in the majority of cases with black oils belonging to the same grade but with different compositions and produced by different manufacturers.

4. Conclusion

The above mentioned enables the conclusion that intensive ultrasonic treatment of the high-viscosity oil products can decrease their viscosity by several times; thereat, the period of relaxation for viscosity of the oil products under the majority of the modes of ultrasonic treatment described in this study takes longer than 10 days. This means that applying ultrasound of high intensity can considerably alleviate the difficulties occurring in the process of extracting and transporting heavy grades of oil due to their high viscosity. It has to be noted that the changes occurring in the viscosity of black oil M-100 in the course of relaxation are of anomalous non-monotone nature that necessitates selecting optimum mode of ultrasonic treatment under the specific conditions of extraction or transportation of heavy oils.

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