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Modification of the Rheological Properties of Heavy Boiler Fuel by Adding Carbon Nanotubes and Dehydrated Carbonate Sludge

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Abstract—The possibilities of reducing the viscosity of heavy fuel oil with an increased proportion of residual fractions through the use of nanomaterials, such as carbon nanotubes (CNTs) and dehydrated carbonate sludge, have been investigated. The results of studying of rheological characteristics of fuel oil and composite fuel containing carbon nanotubes dispersed in an oil-soluble nonionic surfactant (M100 fuel oil + 0.0125 wt % CNT + 0.5 wt % Diproxamine) or dehydrated carbonate sludge (M100 fuel oil + 0.1 wt % carbonate sludge) are presented, as well as their heating value. The existence of a synergistic effect of the combined use of CNTs and carbonate sludge has been established. The possible mechanisms of change in the viscosity of the fuel are considered. It has been shown that carbon nanotubes together with dehydrated carbonate sludge can be most promising for use as heating oil additives, since they reduce fuel viscosity, improve combustion efficiency, and reduce the emission of hazardous gases.

Keywords: petroleum fuel, fuel oil, carbon nanotubes, dynamic viscosity, surfactants

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The issues of improving the quality of fuel oil and the efficiency of its combustion are of particular relevance due to the increase in the share of heavy residual fractions in the fuel as a result of enhancing oil refining efficiency [1]. Various performance characteristics of fuel can be improved by introducing special additives into them. The use of additives not only makes it possible to control low-temperature corrosion, but also can lead to a decrease in the viscosity of boiler fuel, thereby reducing energy costs of its pumping through pipelines, unloading from tanks, and feeding into the boiler, and therefore is of fundamental importance from the viewpoint of energy saving. Some additives can also enhance the fuel combustion efficiency and reduce the toxicity of flue gases, facilitating environmental improvement.

Nanotechnology methods and nanomaterials have been recently used to create unconventional oil and fuel additives [2–4]. To improve the rheological properties of liquid multicomponent systems, which include fuel oil, small additives of nanoparticles of any nature, including carbon nanotubes, can be used [5, 6]. A study of concentration dependence curves for the viscosity of liquid heterogeneous systems revealed the presence of minima at a certain sufficiently low concentration of nanoparticles [7]. To explain the effects of viscosity reduction observed in such systems in the presence of nanoparticles, various mechanisms suggesting a change in the morphology of the composite and transition to stratified flow have been proposed [8, 9].

The existing experience of using nanoparticles to improve the rheological, performance, and environmental characteristics of diesel and biodiesel fuel [10–14] provides reasons to explore the possibility of using carbon nanomaterials to improve the performance of organic boiler fuel (BF), including application with other nanostructured additives that have already proven their effectiveness. It should be noted that carbon nanotubes (CNTs) despite the fact that they are not biodegradable nanoparticles, completely burn together with the fuel, since they consist of pure carbon, and their catalytic properties lead to more complete combustion of other fuel components and a noticeable reduction in emissions of hazardous gases [12, 13], an improvement that may turn important for eliminating the negative effects of the use of heavy fuel. In particular, some studies reported recently (see, e.g., [12–14]) have revealed that using CNTs (together with CeO_2 in some cases) as an additive for diesel and biodiesel fuels improves all engine operating parameters and significantly reduces emissions of the hazardous gases NO_x and CO by 19–45 and 39–50%, respectively, and unburned hydrocarbons (HC) and soot by 60–71%. A similar approach can be applied to alter the characteristics of a heavier boiler fuel.

The purpose of this work is to explore the possibility of improving the rheological properties and performance of fuel oil by adding carbon nanotubes and other nanostructured entities and to determine the degree of reduction in viscosity of the resulting composite fuel.

EXPERIMENTAL

The nanoscale additive used was multiwalled carbon nanotubes (CNTs) of the Taunit carbon nanomaterial (http://www.nanotc.ru) dispersed in an aqueous dispersion of sodium dodecyl sulfate (SDS, anionic surfactant) with a concentration of 100 mmol/L and in Diproxamine (oil-soluble liquid nonionic surfactant). The selection of these surfactants was due to their availability and the authors' experience of operating with them [15–18], including their use as a boiler fuel additive [16–18].

In addition, to improve the physicochemical properties of fossil fuel, we used dehydrated carbonate sludge as an additive. Since nanoparticles of many elements (aluminum, iron, magnesium, copper, boron, manganese, calcium, and cerium), as well as their oxides [11], turned out to be effective as diesel fuel additives [11], we assumed that such additives could be replaced to some extent by the waste generated by coagulating and liming of natural waters during water treatment at thermal power plants. Dehydrated carbonate sludge has a diverse chemical composition (calcium carbonates, magnesium and iron hydroxides, aluminum compounds, etc.) and has high dispersity and surface activity due to high porosity resulting from water evaporation. Therefore, during the dewatering process, the composition and structure of the carbonate sludge particles become similar to those of nanoparticles used to improve the performance of diesel fuel. As a boiler fuel additive, we used a finely divided fraction of dehydrated carbonate sludge of water treatment at Kazan CHPP-1.

Samples of high-sulfur fuel oil of the M100 brand, produced by the Nizhnekamsk refinery and used at the Kazan combined heat and power plant as emergency and backup fuel, were taken as boiler fuel. It should be noted that studying the viscosity of fuel oil samples and water–fuel emulsions with additives prepared on the basis of these samples, we came across different values of viscosity and fundamentally different types of its dependence for particular samples of fuel oil of the same M100 brand taken at different times from different sources. This fact undoubtedly complicates the description of the processes occurring in the presence of nanostructured entities added to the fuel and has an effect of its own on reproducibility of the results.

Our previous experiments on studying the rheological properties of fuel oil with an admixture of carbon nanotubes dispersed in aqueous solutions of the anionic surfactant sodium dodecyl sulfate proved the fact of viscosity reduction by introducing a rather large amount of CNTs (0.82 wt %) [16]. Using carbon nanotubes in such concentrations is uneconomical. Therefore, was chose the oil-soluble nonionic surfactant Diproxamine-157 manufactured by Kazanorgsintez (http://www.kazanorgsintez.ru), which is one of the commonly used demulsifiers and paraffin deposition inhibitors, as a more appropriate dispersion medium for CNTs. The choice of this surfactant for dispersing CNTs is also due to the fact that the use of Diproxamine as an additive to heavy boiler fuel in some cases may lead to an improvement in its rheological characteristics [18], although this effect is not clearly manifested for the samples studied in this work (Figs. 1a, 1b). Moreover, as shown in Fig. 1a, the dynamic viscosity of fuel oil increases in the presence of Diproxamine.

To ensure reproducibility of the results, two different samples of M100 fuel oil from different sources were taken for the study. These samples, as well as a composite fuel prepared on their basis (fuel oil M100 + 0.0125 wt % CNT + 0.5 wt % Diproxamine), were studied using a Rheomat RM 100 rotary viscometer. The angular velocity of the cylinder varied from 50 to 300 s^{-1}. The torque proportional to the tangential stress in the annular gap was determined and was converted into an electrical signal. Viscosity values were calculated using a built-in microprocessor analyzing changes in torque and shear rate. The operation of the viscometer was controlled from a personal computer through the VISCO-RM SOFT software. The results of determination of the dynamic viscosity of fuel oil and the composite fuel, which was a mixture of M100 fuel oil with a suspension of carbon nanotubes in Diproxamine, are shown in Fig. 1.

Figure 2 shows the dependence of the dynamic viscosity of samples of pure M100 fuel oil (solid line) and the fuel oil with an admixture of another nanostructured additive, carbonate sludge (0.1 wt %), on shear rate at two temperatures of (a) 65 and (b) 70°C.

The rheological characteristics of the fuel oil and the composite fuel, made by mixing the M100 fuel oil with a suspension of carbon nanotubes in Diproxamine and added carbonate sludge (Fig. 3), i.e. containing both of the additives simultaneously, were also studied.

In addition to the viscosity characteristics of BF samples, we determined the lower (net) calorific value of both M100 fuel oil from the Nizhnekamsk refinery and the composite fuel prepared on its basis. The measurements were carried out according to GOST 21261-91 by burning fuel in an ABK-18 type I

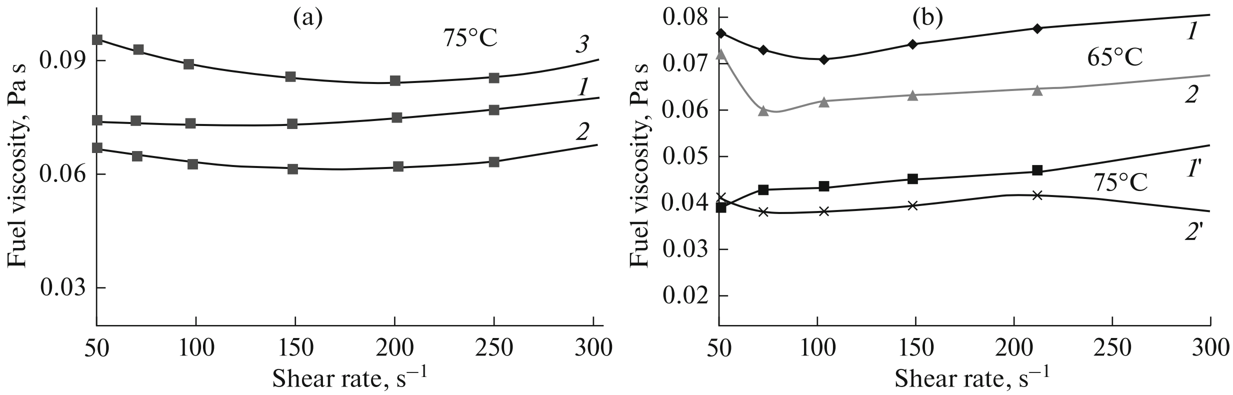

Fig. 1. Dependence of dynamic viscosity on shear rate for two different samples (a) and (b) of M100 fuel oil: (*1*, *1*') are neat fuel oil at two temperatures, (*2*, *2*') fuel oil + 0.0125 wt % CNT + 0.5 wt % diproxamine, and (*3*) a mixture of fuel oil with diproxamine (0.5 wt %).

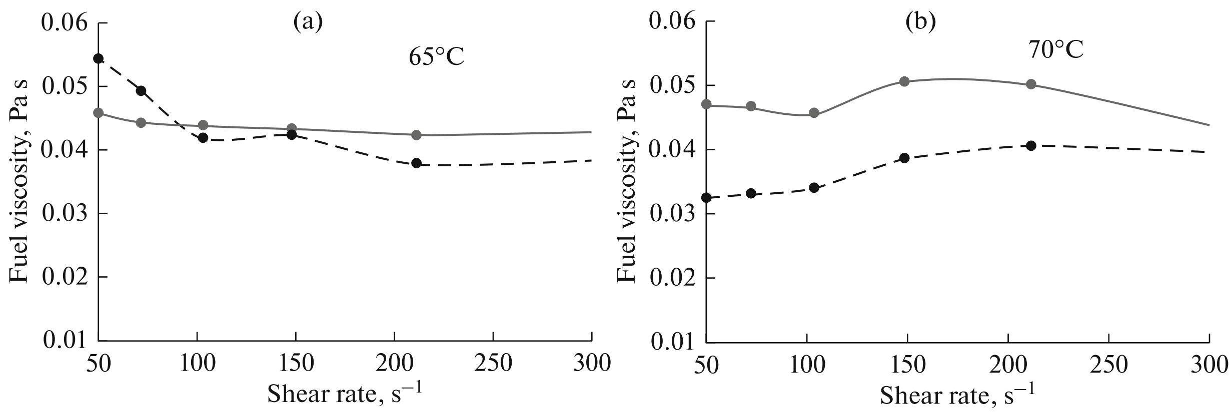

Fig. 2. Dependence of the dynamic viscosity of samples of neat M100 fuel oil brand (solid line) and the fuel oil with an admixture of 0.1 wt % carbonate sludge (dashed line) on shear rate at temperatures of (a) 65 and (b) 70°C.

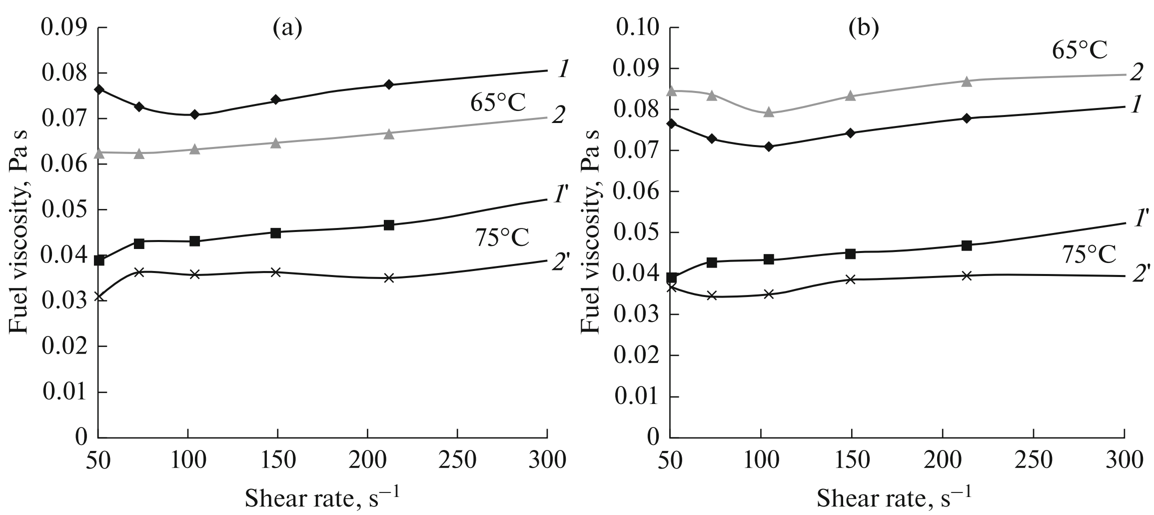

Fig. 3. Dependence of dynamic viscosity on shear rate for fuel samples based on M100 fuel oil: (*1*, *1*') neat fuel oil and (*2*, *2*') fuel oil + 0.0063 wt % CNT + 0.25 wt % diproxamine + 0.5 wt % carbonate sludge in case (a) or fuel oil + 0.0125 wt % CNT + 0.5 wt % diproxamine + 0.5 wt % carbonate sludge in case (b) at temperatures of 65 and 75°C.

Table 1. Lower calorific value (as fired) of composite fuel

No.	Fuel calorific value, kJ/kg	Type of composite fuel
1	41867	Neat M100 fuel oil
2	38946	M100 fuel oil + 0.1 wt % carbonate sludge
3	42179	M100 fuel oil + 0.0125 wt % CNT + 0.5 wt % Diproxamine + 0.1 wt % carbonate sludge

bomb calorimeter in the isothermal mode. The calorific value of the fuels was determined in the ABK-18 calorimeter for three samples: (1) neat M100 fuel oil, (2) fuel oil with an 0.5 wt % admixture of dehydrated carbonate sludge, and (3) fuel oil containing 0.0063 wt % CNT + 0.25 wt % Diproxamine + 0.5% wt % dehydrated carbonate sludge as additives . The results of the tests are shown in Table 1.

RESULTS AND DISCUSSION

The obtained results are described well by the concept, proposed in [18] for bitumen and developed further in [5, 6], of the appearance of additional structuring of the dispersion medium around nanoparticles in liquid heterogeneous systems. According to this concept, nanoparticles (in our case, carbon nanotubes or carbonate sludge) begin to play the role of structure-forming centers, around which ordered layers of components of the matrix material (HC molecules) are formed by the action of excess surface energy of the nanoparticles. This means that supermolecular structuring occurs near the nanoparticles. At some sufficiently low concentration of nanoparticles, almost complete structuring occurs in the bulk of the sample. In this case, liquid multicomponent systems are a combination of supramolecular entities separated by thin layers of the remaining less dense part of the dispersion medium. Thus, it is on this layer that the slip plane from the applied strain will appear, leading to the emergence of layer-by-layer shear flow and, hence, a sharp decrease in viscosity for a small concentration range. The nature of the change in viscosity of sample **a** (Fig. 1a) suggests the absence of adhesion between the supramolecular entities. For sample **b** (Fig. 1b), a small adhesion is already observed, but a mechanical action leads to the destruction of bonds between the resulting supramolecular entities already at low speeds (about 70 s^{-1}). In both cases, the observed decrease in viscosity was approximately 10%.

With a further increase in the concentration of nanoparticles, adhesion of the supramolecular entities should occur, which is manifested in an increase in the kinematic viscosity. Thus, when determining the optimal concentration of nanoparticles for viscosity reduction, it is important to get into a certain concentration range, which depends on the type of both nanoparticles and the dispersion medium and varies from 0.001 to 0.5 wt % for carbon nanotubes according to different data [7, 19]. In particular, the decrease in the viscosity of fuel oil in our case corresponded to the concentration range of carbon nanotubes near 0.0125 wt %. Note that preliminary dispersion of CNTs in oil-soluble Diproxamine for use in fuel oil was much more effective than their dispersion in aqueous sodium dodecyl sulfate solutions.

Approximately the same behavior of viscosity was observed in the presence of the other nanostructured additive, microparticles of dehydrated carbonate sludge (Figs. 2a, 2b). Compounds making up the sludge form a nano- and micrometer-sized structure, initially separated by water molecules. During the dehydration process, the composition and structure of carbonate sludge particles become close to those of nanostructured entities. Accordingly, the mechanism of their effect on the viscosity properties is similar to that of nanoparticles, although the working concentrations are much higher in this case.

The choice of the carbonate sludge as an additive was based on the previously obtained good results for improving the rheological properties of fuel oils by using this additive [17, 18] with a concentration of 0.5 wt %, which was found to greatly increase the ash content of fuel oil. In this study, preference was given to an additive concentration of 0.1 wt %. In this concentration, the additive reduces the viscosity of fuel oil, lowers its pour point, decreases the sulfur content in emissions, and improves the structure of deposits, increasing insignificantly the ash content of fuel oil. The results of industrial tests that we conducted on the basis of the Naberezhnye Chelny CHPP show a decrease in the weight fraction of sulfur oxides emission by 36.5% [20].

We also measured the viscosity of a composite fuel in the presence of both of these additives (M100 fuel oil + 0.00625 wt % CNT + 0.25 wt % Diproxamine + 0.5 wt % carbonate sludge). This sample showed the best results (Fig. 3a), exhibiting a synergistic effect of the combined use of carbon nanotubes and carbonate sludge. Note that the concentration of the additional pricing components Diproxamine and CNTs in this sample is halved (with the same viscosity reduction effect). We observed a decrease in viscosity even at low shear rates, a behavior that suggests the absence of explicit structuring in the hydrocarbon medium. From the data in Fig. 3b it can be seen that in the presence of carbonate sludge, the addition of carbon nanotubes up to concentrations specified in Fig. 1 (0.0125 wt %)

begins to interfere with the decrease in viscosity at 65°C, although the decrease is still observed at a higher temperature of 75°C. This fact also indicates the presence of the synergistic effect of CNTs used together with carbonate sludge and suggests that the concentration range of added nanoparticles, corresponding to a decrease in viscosity, depends not only on the type of dispersion medium and type of nanoparticles used, but also on the temperature of the mixture. Structuring is more intense at lower temperatures.

The determination of the lower calorific value as fired for the M100 fuel oil from the Nizhnekamsk refinery and the composite fuel prepared on its basis revealed the following results. Compared to the neat fuel oil, the addition of carbonate sludge reduced the heating value of the fuel oil by about 5%. However, its use leads to undeniable environmental benefits, namely, reducing sulfur oxide emissions by 36.5% [20]. Therefore, the use of carbon nanotubes together with dehydrated carbonate sludge appears to be most promising in our opinion. In this case, the calorific value becomes higher than that of neat fuel oil. It should also be expected that the use of such a composite fuel will also lead to improved environmental performance.

In summary, we have explored the possibility of reducing the viscosity of fuel oil by using the nanomaterials carbon nanotubes and dehydrated carbonate sludge. It has been found that the rheological properties of the composite fuel containing small additives of these substances: M100 fuel oil + 0.0125 wt % CNT + 0.5 wt % Diproxamine, M100 fuel oil + 0.1 wt % carbonate sludge, and M100 fuel oil + 0.0063 wt % CNT +0.25 wt % Diproxamine + carbonate sludge, are improved. The existence of a synergistic effect of the combined use of CNTs with carbonate sludge has been shown. The possible mechanisms of change in viscosity of the fuel are considered. It has been shown that the use of carbon nanotubes together with dehydrated carbonate sludge may be the most promising. Such additives not only ensure a greater calorific value of fuel oil, but also suggest a significant reduction in the emission of hazardous gases. Consequently, the use of such a composite fuel can lead to a decrease in viscosity of the fuel, an increase in the heating value, an improvement in the completeness of its combustion, and as enhancement of environmental performance.

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REFERENCES

1. E. R. Zvereva and T. M. Farakhov, *Energy-Saving Processes and Equipment of Fuel Oil-Fired TPPs* (Teplotekhnik, Moscow, 2012) [in Russian].
2. A. M. Danilov, *Application of Fuel Additives* (Khimizdat, St. Petersburg, 2010) [in Russian].
3. V. M. Kapustin, *Petroleum-Based and Alternative Fuels with Additives* (KolosS, Moscow, 2008) [in Russian].
4. *Nanomaterials and Nanotechnologies in Power Industry*, Ed. by E. V. Shamsutdinov and O. S. Zueva (KGEU, Kazan, 2014) [in Russian].
5. E. R. Zvereva, O. S. Zueva, and R. V. Khabibullina, J. Eng. Appl. Sci. **11**, 2950 (2016).
6. E. R. Zvereva, O. S. Zueva, and R. V. Khabibullina, in *Proceedings of XXIII Al-Russia Conference on Structure and Dynamics of Molecular Systems* (IFKhE RAN, Moscow, 2016) [in Russian].
7. A. A. Pykhtin, P. V. Surikov, L. B. Kandyrin, and V. N. Kuleznev, Vestn. MITKhT **8** (4), 113 (2013).
8. V. G. Kulichikhin, A. V. Semakov, V. V. Karbushev, et al., Polym. Sci., Ser. A **51**, 1303 (2009).
9. A. Ya. Malkin and V. G. Kulichikhin, Usp. Khim. **84**, 803 (2015).
10. V. A. M. Selvan, R. B. Anand, and M. Udayakumar, Fuel **130**, 160 (2014).
11. T. Shaafi, K. Sairam, A. Gopinath, et al., Renew. Sust. Energ. Rev. **49**, 563 (2015).
12. A. I. El-Seesy, A. K. Abdel-Rahman, M. Bady, and S. Ookawara, Energy Procedia **100**, 166 (2016).
13. J. S. Basha and R. B. Anand, Alexandria Eng. J. **53**, 259 (2014).
14. M. Mirzajanzadeh, M. Tabatabaei, M. Ardjmand, et al., Fuel **139**, 374 (2015).
15. O. S. Zueva, O. N. Makshakova, B. Z. Idiyatullin, et al., Izv. Akad. Nauk, Ser. Khim, No. **5**, 1208 (2016).
16. E. R. Zvereva, O. S. Zueva, R. V. Khabibullina, et al., Khim. Tekhnol. Topl. Masel, No. **5**, 15 (2016).
17. E. R. Zvereva, O. S. Zueva, and R. V. Khabibullina, Mater. Sci. Forum **870**, 666 (2016).
18. E. R. Zvereva, G. R. Mingaleeva, R. V. Khabibullina, and G. R. Akhmetvalieva, Pet. Chem. **56**, 65 (2016).
19. T. V. Mokochunina, Candidate's Dissertation in Engineering (Moscow, 2015) [in Russian].
20. E. R. Zvereva, A. V. Dmitriev, M. F. Shageev, and G. R. Akhmetvalieva, Therm. Eng. **64**, 591 (2017).

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