Change in Rheological Properties of Liquid Multicomponent Systems, Including Hydrocarbon Fuel by the Addition of Nanomaterials

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Abstract. The addition of nanostructures leads to a radical transformation of the properties of traditional materials, practically without changing their chemical composition, only due to the tendency of molecules to appearance of the ordered structures and, as a consequence, to a change in functional characteristics of the original materials. Structural ordering of atoms around nanoparticles can lead to a change in viscosity and can be used to reduce the material intensity, the energy intensity, the labor intensity and the cost of production in technological processes. Thus methods and materials of nanotechnology can be used to create a composite hydrocarbon fuel with improved rheological characteristics. To reduce the viscosity of various types of hydrocarbon fuel, small amounts of nanoparticles can be added leading to an additional structure formation which may result in a change in rheological properties due to transition to layerwise shear flow. The possibilities of using carbon nanotubes and dehydrated carbonate sludge of water treatment were analyzed. The presence of a synergistic effect in the joint application of carbon nanotubes with carbonate sludge has been established. It has been shown that the choice of corresponding nanoparticles and their dispersion medium for a particular type of hydrocarbon fuel can significantly improve its rheological characteristics.

1. Introduction
Viscosity is an extremely important operational parameter that determines the course of various technological processes. Reducing in viscosity can lead to a simplification of the technological stages of using of the materials in question, and increase in viscosity may indicate a hardening modification of the materials. A significant influence on the physicochemical properties of various liquid multicomponent systems can be provided by small additions of nanoparticles of any nature. The addition of nanostructures leads to a radical transformation of the properties of traditional materials practically without changing their chemical composition due to the tendency of molecules to self-organize and to self-assembly in the presence of nanostructures. Structural ordering of molecules around nanoparticles in liquid media leads to a change in the functional characteristics of the initial materials and can be used to reduce the material intensity, energy intensity, labor intensity and cost of production in technological processes.
In particular there are data on the effect of nanoparticles in the viscosity characteristics of solutions and melts of polymers [1-5], dispersions based on epoxy oligomers [6], cement mortars [7], low-molecular liquids and oils [8], bitumens [9, 10], as well as diesel and biodiesel fuels [11-18]. The effect of reducing the viscosity of liquid fuel oil (boiler oil, water-fuel emulsions and coal-water slurry fuels) [19-24] can contribute to a reduction in energy costs when it is pumped through pipelines, unloaded from cisterns and fed to the boiler, and therefore of fundamental importance for energy efficiency. It is known that nanoparticles are already use in the case of diesel and biodiesel fuels to improve its viscosity and performance properties [11-18]. The purpose of this work was a theoretical and experimental study of the feasibilities of a purposeful change in the viscosity properties of multicomponent systems, including hydrocarbon fuels, in the presence of small additions of nanoparticles (carbon nanotubes and dehydrated carbonate water treatment sludge).

2. Materials and methods

It is known that nanoparticles are quite expensive formations, the use of which can harm the environment. Therefore, as nanoparticles, we chose carbon nanotubes (CNTs) which have already been used with great success in various fields of energy and are completely burned together with fuel since they consist of pure carbon. For the experiments we chose multi-walled carbon nanotubes of carbon nanomaterial Taunit (Nanotekhtsentr, Tambov, http://www.nanotec.ru), characterized by their relative cheapness and availability. For better dispersion the samples at a temperature of 40 °C for 15 minutes were sonicated at a frequency of 15 kHz in a water bath of Bandelin SONOREX TK52 ultrasonic disperser. Their length after the dispersing in the average ranges from 50 nm to 500 nm with a mean nanotube diameter of 15-20 nm [25]. For dispersion of carbon nanotubes into heavy fuel oil anionic surfactant sodium dodecyl sulfate (SDS, Sigma, L4509) and nonionic surfactant diproksamin-157 (http://www.kazanorgsintez.ru) has been used. Nonionic surfactant diproksamin commonly is used as paraffin inhibitor and demulsifier in the oil and petrochemical industry.

Particles of dehydrated carbonate sludge are another kind of used particles that can reduce harmful emissions into the atmosphere [26] and change the rheological properties of fuel. Dehydrated carbonate sludge is a waste of the process of chemical water purification of water treatment facilities of boiler houses and TPPs. Additives of microparticles of dehydrated carbonate sludge which is waste generated during coagulation and liming of natural waters in thermal power plants to some extent can replace additives of expensive nanoparticles. Carbonate sludge is a product obtained by chemical precipitation. It has a complex of specific physicochemical properties due to a diverse chemical composition (calcium carbonates, magnesium and iron hydroxides, aluminum compounds, etc.). Small carbonate sludge particles have a unique structure characterized by high dispersion, porosity and surface activity. In its structure and qualities, dehydrated carbonate sludge due to the large number of pores that have arisen during its dehydration can be attributed to nanostructural formations.

Samples of high-sulfurious fuel oil (brand M100, production of the Nizhnekamsk oil refinery) have been studied. This fuel oil is applied at Kazan TPPs as reserve and emergency fuel.

As a model system that allows investigating the rheological properties of alternative fuels such as coal-water slurry fuel (CWSF), a liquid coal-water suspensions prepared on the basis of Kuznetsk lean coal ware taken. Suspensions containing 40% of coal and 60% of water either 30% of coal and 70% of water have been investigated. For preparation of coal-water suspension samples crushed coal was sent to the vibratory mill for grinding. The resulting coal dust was sifted into different fractions with the various sizes of coal particles. On the basis of a certain fraction of coal particles, a coal-water suspension samples were prepared. For the addition to coal-water slurry fuel 0.5 g carbon nanotubes were dispersed in 10 ml of 100 mM aqueous solution of anionic surfactant sodium dodecyl sulfate, SDS. Then the samples at a temperature of 40 °C for 20 minutes were sonicated at a frequency of 15 kHz in a water bath of ultrasonic disperser. The use of diproxamine for dispersing of CNT impaired the viscosity properties of water-coal suspensions.
The dynamic viscosity of various types of fuel oils has been investigated using a rotational viscometer Rheomat RM 100. The conditional viscosity (in Engler's degrees, °E) was determined with the aid of the Engler viscometer VU-M-PHP.

3. Experimental
In this paper we investigated the effects of nanostructural formations, such as carbon nanotubes in surfactant dispersions or dehydrated carbonate sludge, in the viscosity characteristics of various types of hydrocarbon fuels. At the same time we tried to analyze the changes occurring in multicomponent fuel systems depending on the concentration of added nanoparticles, their dispersion medium, and temperature. In particular we investigated [20] the rheological behavior of M100 brand fuel oil samples and water-fuel emulsions prepared on its basis with the addition of a 20% SDS aqueous dispersion (concentration of 100 mM) with carbon nanotubes (0.41 wt.% and 0.82 wt. %) and without them on the shear rate at different temperatures (Fig. 1).

![Figure 1. Dynamic viscosity of M100 brand fuel oil samples and water-fuel emulsions prepared on its basis on the shear rate at different temperatures: (1) - pure fuel oil; (2) - fuel oil + 20% water 100 mM SDS dispersion; (3) - fuel oil + 20% CNT suspension in 100 mM SDS dispersion (0.41 wt.% CNTs); (4) - black oil + 20% CNT suspension in 100 mM SDS dispersion (0.82 wt.% CNTs).](image1)

As the examples of multicomponent fuel systems with the same concentration of nanoparticles, but dispersed in different surfactants, we studied two samples of CWSF and showed the existence of a very strong influence of the dispersion medium (Fig. 2). In particular, the use of a nonionic surfactant (diproxamine) led to a sharp increase in the viscosity of CWSF, while the use of anionic surfactant (SDS) significantly reduced its viscosity.

![Figure 2. The dependence of dynamic viscosity of 1) pure CWSF, 2) CWCF + 0.5 wt. % diproksamin (a) or carbonate sludge (b), 3) SWCF + 0.0125 wt.% CNTs dispersed by diproksamin, 0.5 wt. % (a) or by 100 mM SDS solution (b) on the shear rate.](image2)
The effect of different concentrations of nanoparticle additives was analyzed by us in the study of the concentration dependencies of the conditional viscosity of fuel oil samples with the addition of CNT dispersed in diproksamin [21], as well as CWSF samples with the addition of carbon nanotubes and carbonate sludge (Fig. 3).

![Figure 3](image)

**Figure 3.** The dependence of conditional viscosity of coal-water slurry fuel prepared on the basis of various fractions of coal particles (0.125 and 0.01 mm) on concentration of carbonate sludge.

### 4. Results and discussion

Assuming the possibility of improving the properties of heavy fuel oil, we investigated the effect of nanoadditives in the viscosity of boiler oil. Based on M-100 fuel oil samples, water-oil emulsion samples were prepared which containing various concentrations of carbon nanotubes dispersed in an aqueous dispersion of an anionic surfactant [24].

At a carbon nanotube concentration of 0.41 wt. % we obtained contradictory results, and at a concentration of 0.82 wt. % we observed an improvement in the fluidity of fuel oil by 11-26%. However, because of their relatively high cost, carbon nanotubes are not profitable in such concentrations, the result obtained was only of fundamental importance.

The better results were achieved by adding carbon nanotubes dispersed not in an aqueous solution of an ionic surfactant but in a oil-soluble nonionic surfactant – diproksamin (0.0125 wt. % CNTs + 0.5 wt.% diproksamin) [21]. The addition of carbonate sludge revealed the presence of a synergistic effect when used together with carbon nanotubes [22]. This effect allows you to reduce the concentration of the main pricing additive - CNTs.

When studying the rheological properties of another class of multicomponent systems - samples of coal-water slurry fuel, prepared on the basis of lean coal from the Kuznetsk deposit (40% of coal and 60% of water) with the addition of carbon nanotubes at a concentration of 0.0125% we have noticed the significant influence of the nanoparticles dispersing medium. Thus when they are dispersed in nonionic surfactant – diproksamin the viscosity of CWSF samples increases significantly, and when dispersed by 100 mM SDS solution the viscosity significantly reduced. The use of CNTs at low concentrations for such a significant decrease in viscosity (by 1.5-2 times) is economically justified. However coal-water slurry fuel is an extremely complex system, its rheological behavior depends not only on the chemical, but also on the fractional composition of coal particles, and the results are not always reproducible.

The viscosity changes observed for heavy fuel oil and liquid coal-water slurry fuel with the addition of nanostructured formations are explained by appearance of additional structure formation in the dispersion medium around the nanoparticles in liquid. Such structurization leads to the appearance of a layerwise shear flow and, accordingly, to reduce in the viscosity for a small region of nanoparticle concentrations. According to this concept the region of viscosity decrease correspond to low
concentrations of nanoparticles. The best results for M100 fuel oil, which we observed, corresponded to the concentrations of CNTs of the order of 0.0125 wt. % (in diproxamine) [21]. The same concentrations proved to be optimal for CWSF when dispersed using SDS. A study of the concentration dependences of the viscosity of CWSF with the addition of carbonate slurry revealed the existence of a minimum of the conditional viscosity observed at a slurry concentration equal to 0.3 wt.%. Here it should be noted one feature – the increase in viscosity in the range of low concentrations of this additive, associated with the absorption and binding of water by the sludge particles. However, a further increase in the slurry concentration leads to a decrease in the viscosity of the fuel.

The conducted experiments clearly showed the dependence of the properties of multicomponent systems not only on the kind of the nanoparticles used and their concentration, but also on the type of surfactants in which they are dispersed, and hence on the supramolecular structure of the CNTs-surfactant complexes and their interaction with the dispersion medium.

5. Conclusion
In this paper we have shown that by nanoparticles adding it is possible to control the viscosity of multicomponent systems. In particular, it has been established that the use of the concept of additional structure formation for predicting the behavior of fuel dispersed systems in the presence of nanoparticles makes it possible to significantly narrow the search for optimal concentrations of additives of the components under consideration. The choice of fitting nanoparticles and their dispersion medium for a particular type of hydrocarbon fuel makes it possible to reduce its viscosity by 15-25%.

6. References
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