Journal of Engineering and Applied Sciences 11 (Special Issue 1): 2950-2954, 2016
ISSN: 1816-949X

Nanomaterial Effect Study in the Viscosity Characteristics of Fuel Oil and Alternative Fuels Used at Fuel and Energy Complex Enterprises

E.R. Zvereva, O.S. Zueva, R.V. Khabibullina and A.O. Makarova
Kazan State Power Engineering University, Krasnoselskaya Str., 51, Kazan, Russia

Abstract: The changes in viscosity characteristics of fuel oil and coal-water slurry fuel as well as biofuel precursors-polysaccharide aqueous solutions with the addition of nanoparticles-carbon nanotubes have been considered. A theory describing the experimental data and predicting the existence of reduction in the viscosity over a range of nanoparticle concentrations has been presented. It was shown that one of the reserves for hydrocarbon fuel rheological property improvement is the determination of nanoparticle concentration leading to viscosity reduction of a certain type of liquid fuel at their operating temperatures and the use of nano-additives within the required concentration range.

Key words: Hydrocarbon fuel, fuel oil, coal-water fuel, viscosity, rheological properties, nanoparticles, carbon nanotubes

INTRODUCTION

In recent years they noted a significant effect of small nanoparticle additives of any nature on the physical-chemical properties of multi-component systems in the liquid state in particular on the viscosity characteristics of the hydrocarbon fuel, bitumen, polymer melts and solutions, cement mortar, etc., (Shaafi *et al*., 2015; Borisova *et al*., 2015). Viscosity is a very important performance parameter that contributes to the progress of various technological process at the enterprises of fuel and energy complex. Viscosity reduction leads to the simplification of material use technological stages in many cases and the viscosity increase may represent the reinforcing modification of materials by nanoparticles. The degree of rheological property change and the optimum concentration value (in many cases these are the portions of a percent or less) at which such phenomena may occur, depend on the type of nanoparticles and the physical-chemical properties of the used media.

The effects of viscosity reduction at a certain content of nanoparticles were observed in the liquid precursors of nanocomposite materials (Kulichikhin *et al*., 2009). In the case of polymer melts (solutions) they were observed for elastomers filled with soot or aerosi. They were noted with the introduction of a certain number of Na-montmorillonite particles and the nanodiamonds of detonation synthesis (Kulichikhin *et al*., 2009) in the melt of various polymeric matrices, etc. In order to explain the observed effects different mechanisms were proposed for viscosity reduction explaining the composite morphology change and the transition to the stratified flow (layer by layer) (Malkin and Kulichikhin, 2015; Kulichikhin *et al*., 2009). Shitov *et al*. (2014) studied the addition of carbon black, carbon nanotubes and aerosil leading to viscosity property change of polymeric composite materials based on epoxy oligomer and low molecular weight liquids. The presence of minima on the concentration dependence curves of considered liquid viscosity and the dependence of minimum location on dispersion medium type and a dispersed phase for all examined cases. The study of dispersion optical density providing the information on the aggregation processes allowed to make the conclusion that in the studied concentration range in the fluid around nanoparticles the sedimentation stable area of supramolecular nanoscale (100-200 nm) structural formations is developed. The flow of liquid multicomponent systems at the presence of such formations may take place by the division of layers with different viscosity, i.e., a stratified shear flow may occur. Karpushkin *et al*. (2014) and Zhiteneva *et al*. (2012) also noted the additional structure formation in polyacrylonitrile solutions and viscosity reduction to 1.5 times.

Similar phenomena were observed in the process of construction mixture nanomodification, where the addition of carbon nanostructures (fullerenes, carbon nanotubes, amorphous carbon) contributed (according to the researchers opinion (Yasinskaya *et al*., 2011) to the formation of fractal percolation networks and a specific structure formation of water, providing a solution morphology change. The nanostructuring of mixed water

---

Corresponding Author: E.R. Zvereva, Kazan State Power Engineering University, Krasnoselskaya Str., 51, Kazan, Russia by a nanomodifier on the basis of carbon nanostructures decreased the viscosity of the cement paste in 1.4-1.7 times. The viscosity change was observed with the addition of nanoparticles for various refinery products. The reduction of viscosity was observed for diesel fuel with the addition of nanoparticles (Shaafi *et al*., 2015) including the carbon nanotubes and it attains a particular importance for heavy fuel oil because it can give a significant economic effect. The reduction of fuel oil viscosity, providing their better pumpability through pipelines, allows to reduce its heating intensity at the stage of preparation for burning and thereby reduce the energy costs for its heating. Zvereva *et al*. (2016a, b), Laptev *et al*. (2011) showed that the addition of carbon nanomaterial “Taunit” and dewatered carbonate sludge for HPS water treatment with diverse chemical composition, high dispersion and surface activity at the concentration of additive in the fuel oil close to 0.5 wt. % leads to viscosity decrease by 7-25% viscosity which provides energy efficiency increase and fuel economy.

The rheological properties of other petroleum products-bitumen and petroleum oils as well as the possibilities of their modifying by carbon nanoscale structures were discussed in many articles in particular by Ilyin *et al*. (2014) and Trukhina *et al*. (2013) to improve operational properties. It should be noted that the appearance of modified bitumen reinforcing action used in the production of asphalt concretes is not associated not with the decrease but with the increase of their viscosity properties (relative to a minimum). Let’s note that in all these studies they note the appearance of nanoscale supramolecular structures in a liquid, whose sizes are measured in the range of 100-1000 nm, leading to the change of fluid rheological properties.

Issue theory: Ilyin *et al*. (2014) and Trukhina *et al*. (2013) in order to explain the observed effects, they put forward the concept of reinforcing modification of various materials by nanoparticles. In our opinion a put forward concept allows to explain the anomalous rheological behavior of multicomponent systems to a large extent in the presence of nanoparticles. Within this representation nanoparticles act as structure forming centers around which the ordered layers of matrix material components appear, i.e., the supramolecular structures under the influence of the excess surface energy (Zueva, 2016; Zueva *et al*., 2014). At low concentrations of nanoparticles these ordered (and probably, more dense) formations called heterospheres (like hetero epitaxial layers during crystal growth), the size of which is caused as by a dispersion medium, so as by the form of nanoparticles and can reach up to 1 mcm and they do not make the impact on the medium viscosity. In this case, the viscosity is still determined by a dispersion medium. The increase of nanoparticle concentration leads to almost complete structuring in a sample volume at which heterospheres are separated by thin layers of less dense dispersion medium part. At the same time the sliding plane of the applied deformation will be mainly on this layer, resulting in the emergence of stratified shear flow at which heterospheres can still rotate freely and, accordingly in a sharp decrease of viscosity for a small range of concentrations. The subsequent increase of nanoparticle concentration leads to the adhesion of heterospheres and kinematic viscosity increase up to the original and in some cases to higher values.

The impact of shear stress during dynamic viscosity study in the field of heterosphere cohesion should lead at first to the partial destruction of heterospheres and to their complete destruction at high shear rates. This process should be accompanied by viscosity reduction to the values which characterize the dispersion medium.

It should be noted that the concept of heterosphere occurrence can be extended to any liquid multicomponent systems containing nanoparticles, despite of the fact that the forces which lead to aggregation of molecules, may have a different nature depending on considered system composition and complexity, the polarity of its constituent molecules, the presence of particular functional groups in them, etc. While the existence of additional structure formation are conditioned by two factors: the fact of nanoparticle introduction with excess surface energy in the multicomponent system and the possibility of movement and the association of molecules around them due to the liquid aggregate state of a system, the behavior of completely different systems is similar. It should also be noted that the anisotropic shape of nanoparticles (in particular this applies to carbon nanotubes, the length of which in our samples ranges from 50-500 nm at an average diameter of nanotubes of 15-20 nm (Zueva *et al*., 2014, 2016) can lead to an irregular spherical shape. However, all abovementioned considerations remain valid ones except for the capabilities of heterosphere free rotation-in this case you should only expect the turning of formations and their orientation in the direction of force application which do not prevent a shear layer flow. The proposed concept allows to explain the viscosity changes observed by us for various multi-component systems.

MATERIALS AND METHODS

They studied the viscosity properties of heavy fuel oil (black oils) using the example of M100 fuel oil samples and liquid coal-water fuel prepared on the basis of Kuznetsky deposit lean coal containing 40% of coal and 60% of water. The preparation of coal-water suspension samples was carried out as follows. The crushed coal was sent to the vibratory mill for grinding. The resulting coal dust was sifted into different fractions with the dimensions of 0.2; 0.125; 0.09; 0.063; 0.05 mm. The particles with the sizes up to 90 microns were separated on sieves were weighed and fed into a mixer in which water was dosed from a measuring container.

They used as the additives the multiwall Carbon Nano Tubes (CNT) of the carbon nanomaterial “Taunit” (http://www.nanotc.ru), dispersed in the aqueous solutions of Sodium Dodecyl Sulfate (SDS, an anionic surfactant (Borovskaya *et al*., 2016; Gubaidullin *et al*., 2016) and in diproxamine (good nonionic surfactant soluble in oils, http://www.kazanorgsintez.ru) as well as anhydrous carbonate slurry for HPS purification similar to nanoparticles by its structure (Laptev *et al*., 2011; Zvereva, 2016). Dehydrated carbonate slurry as the product obtained by chemical precipitation, has diverse chemical compositions, high dispersion and surface activity. One should note the ecology of all used additives. Even non-biodegradable carbon nanomaterials not only oxidized completely to carbon dioxide but also contribute to a better combustion of the hydrocarbons that make up the fuel. The smples of coal-water fuel, a coal-water mixture with Diproxamine-157 and nanoadditives were tested using the rotational viscometer Rheomat RM 100 to determine the dynamic viscosity at different shear rate values. The determination of the dynamic viscosity consisted in shear stress measuring arising in the studied sample of the hydrocarbon fuel. The angular velocity ranged from 50-300 sec^{-1}. Fuel viscosity measurements were performed at several temperatures in the range of 60-75°C and different shear rates. The viscometer operation was controlled from the PC via the software “VISCO-RM SOFT”.

In order to verify the proposed hypotheses using the Engler’s viscometer VU-M-PHP the viscosity of two more multicomponent systems prepared on the basis of polysaccharides (biofuel precursors) with gel forming properties: an aqueous solution of sodium alginate (1 wt.%) and an aqueous solution of k-carrageenan (1 wt.%) at the temperatures of 30 and 50°C with carbon nanotubes without them.

RESULTS AND DISCUSSION

Some of experimental study results of the considered system viscosity according to shear rate, taking into account the experiment error graphically represented on Fig. 1-4. Unfortunately, the results were obtained for the

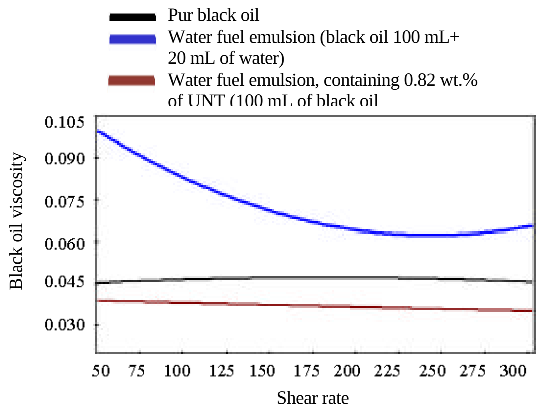

Fig. 1: Dynamic viscosity dependence of M-100 black oil and the mixtures on the basis of shear rate at t = 75°C

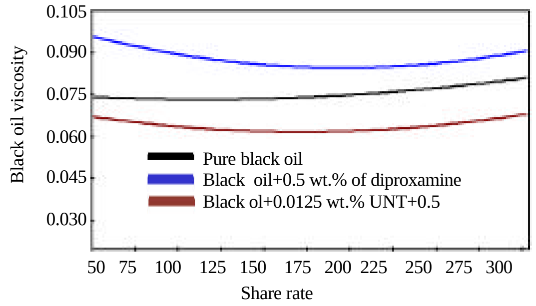

Fig. 2: Dynamic viscosity dependence of M-100 fuel oil samples and its mixtures on the shear rate at t = 75°C

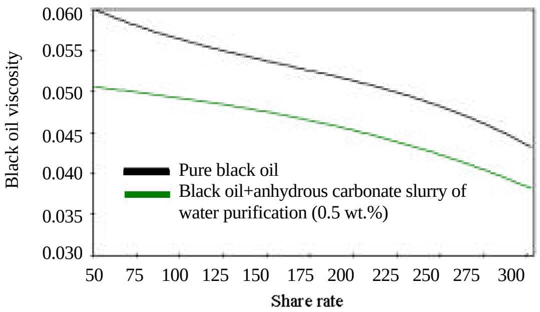

Fig. 3: Dynamic viscosity dependence of M-100 fuel oil samples and its mixtures on the shear rate at t = 75°C

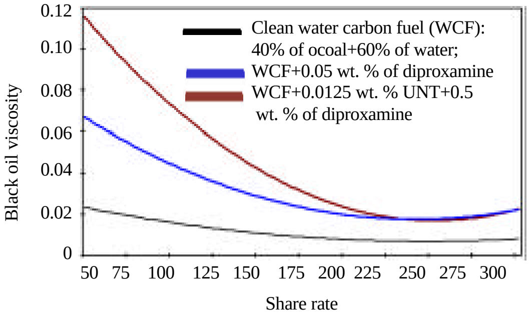

Fig. 4: The dependence of Coal-Water Fuel (CWF) dynamic viscosity and the compositions on the basis of shear rate at t = 60°C

various black oil samples which even under the same brand demonstrate various viscosity values and a different behavior depending on layer movement speed gradient. Therefore, the rheological behavior of the original fuel oil samples is shown in Fig. 1-4.

In this study, we will not analyze the behavior peculiarities of the studied fuel samples with the additives of carbon nanomaterial. Note only the facts, confirming the viscosity change within the concept of heterosphere emergence. The comparison of M100 black oil sample dynamic viscosity and especially water-fuel emulsion and its mixtures with carbon nanotubes dispersed in DSN aqueous suspension, indicates a significant decrease of viscosity (Fig. 1, curve 3) at rather high concentration (0.82 wt.%) of carbon nanotubes which we attribute their dispersion in water which as we know degrade the performance of fuel oil. During the use of a non-ionic surfactant-diproxamine-the viscosity reduction was observed at much lower concentrations (0.0125 wt. %) of nanotubes (Fig. 2, curve 3). At that the addition of pure diproxamine to such an effect does not result in (Fig. 2, curve 2). A similar effect on the rheological properties was provided by the addition (0.5 wt. %) of dewatered carbonate sludge from the chemical water treatment of thermal power plants (Fig. 3).

The dynamic viscosity of coal-water fuel (Fig. 4) showed a completely different behavior. In the presence of carbon nanotubes viscosity was several times higher as compared with the original dispersion medium at low shear rates and significantly decreased with flow velocity increase. This behavior indicated the appearance of an additional structure development throughout the whole volume of the sample observed by the introduction of carbon nanotubes, i.e. the appearance of heterospheres and their adhesion and then their partial destruction with a shear rate increase and the complete destruction of heterospheres at high shear rates. This conclusion is confirmed by the fusion of curve 2 and 3 (Fig. 4) at the speeds greater than 230 $\sec^{-1}$.

Table 1: Viscosity of multicomponent systems at different temperatures

	30 °C	50 °C	30 °C	50 °C
Substance	Without UNT	Without UNT	With UNT	With UNT
Viscosity, °E sodium alginate	12.98	7.38	13.06	8.11
Viscosity,°E κ- carrageenan	7.37	4.46	7.10	4.80

Viscosity (in Engler degrees, °E), determined by Engler's viscometer VU-M-PHP for multicomponent systems prepared on the basis of 1 wt. % of polysaccharide aqueous solution at the temperatures of 30°C and 50°C with carbon nanotubes and without them is shown in Table 1. According to the obtained experimental data, the viscosity of sodium alginate solutions is not reduced in the presence of carbon nanotubes. However the situation is somewhat different in k-carrageenan solutions: if the presence of carbon nanotubes at 50°C does not decrease the viscosity, then their presence reduces the viscosity by almost 4% at 30°C. This fact not only indicates the presence of an additional structure formation in k-carrageenan solutions around the nanoparticles in liquid but also emphasizes the importance of temperature factors in the implementation of such supramolecular changes.

Summary: So in this study, the concept of heterosphere development-an additional structuring of the dispersion medium around the liquid nanoparticles was developed. The presented study of the dynamic viscosity in fuel oils and coal-water fuels and the mixtures with nanoparticle additives on their basis as well as the aqueous solutions of polysaccharides in the presence of carbon nanotubes confirms the acceptance of the experimental data with the basic provisions of the considered theory. The importance of temperature factors was noted during the implementation of supramolecular changes.

Thus, one of the reserves for hydrocarbon fuel rheological property improvement is to determine the concentration of nanoparticles, leading to the viscosity decrease for a particular type of liquid fuel in the range of its operating temperatures and the use of nano-additives in the desired concentration range.

CONCLUSION

During the use of a non-ionic surfactant-diproxamine-the viscosity reduction was observed at much lower concentrations (0.0125 wt.%) of nanotubes, the addition of pure diproxamine did not bring to such an effect. A similar effect on the rheological properties was caused (0.5 wt. %) by the addition of dewatered carbonate sludge from chemical water treatment of thermal power plants.

An opposite behavior was observed for the dynamic viscosity of coal-water fuel. In the presence of carbon nanotubes viscosity had significantly higher values than an original dispersion medium at low shear rates and significantly decreased with flow velocity increase.

According to the obtained experimental data, the viscosity of sodium alginate solutions is not reduced with carbon nanotubes. However, the situation is somewhat different in k-carrageenan solutions: at 30°C the presence of nanotubes results to viscosity reduction by almost 4%.

ACKNOWLEDGEMENTS

The study was supported by RFBR project No. 16-08-00731-a "The improvement of the operational and the environmental characteristics of liquid organic fuel oils by additives including carbon nanotubes".

REFERENCES

Borisova, V.S., D.Y. Shitov, N.S. Dikanova, Y.M. Bydnickiy and S.T. Luu *et al*., 2015. Features of the rheological behavior of nanocomposites based on polyolefins. Adv. Chem. Chem. Technol., 29: 17-19.

Borovskaya, A.O., B.Z. Idiatullin and O.S. Zueva, 2016. Carbon nanotubes in the surfactants dispersion: Formation of the microenvironment. J. Phys. Conf. Ser., 690: 1-7.

Gubaidullin, A.T., I.A. Litvinov, A.I. Samigullina, O.S. Zueva and V.S. Rukhlov *et al*., 2016. Structure and dynamics of concentrated micellar solutions of sodium dodecyl sulfate. Russ. Chem. Bull., 65: 158-166.

Ilyin, S.O., M.P. Arinina, Y.U.S. Mamulat, A.Y.A. Malkin and V.G. Kulichikhin, 2014. Rheological properties of road bitumens modified with polymer and solid nanosized additives. COLLOID. J., 76: 425-434.

Karpushkin, E.A., A.K. Berkovich, M.V. Artemov and V.G. Sergeev, 2014. Rheological properties of polyacrylonitrile solutions containing highly dispersed carbon nanotubes. Poly. Sci. Ser., 56: 681-686.

Kulichikhin, V.G., A.V. Semakov, V.V. Karbushev, N.A. Plate and S.J. Picken, 2009. The chaos-to-order transition in critical modes of shearing for polymer and nanocomposite melts. Polym. Sci. Ser., 51: 1303-1312.

Laptev, A.G., E.R. Zvereva and L.V. Ganina, 2011. Use of water preparation carbonate sludge in fuel oil facilities of thermal power plants. Rans. Academenergo, 1: 55-63.

Malkin, A.Y.A. and V.G. Kulichikhin, 2015. Structure and rheology of highly concentrated emulsions: A modern look. Russ. Chem. Rev., 84: 803-825.

Shaafi, T., K. Sairam, A. Gopinath, G. Kumaresan and R. Velraj, 2015. Effect of dispersion of various nanoadditives on the performance and emission characteristics of a CI engine fuelled with diesel, biodiesel and blends a review. Renewable Sustainable Energ. Rev., 49: 563-573.

Shitov, D.Y., T.P. Kravchenko, V.S. Osipchik and E.G. Rakov, 2014. Composite materials based on polypropylene with carbon nanofillers. Int. Polym. Sci. Technol., 41: T27-T31.

Trukhina, M., G.T. Mokochunina, M. Kuzmin and M. Provorotov, 2013. Study of performance type nanofluids armcap-w and prospects of such products. Nanotech, 2: 48-57.

Yasinskaya, E.V., N.M. Nikulin and E.E. Krivtsov, 2011. Study of characteristics of nano-modified dry building mixes. Mag. Civil Eng., 2: 29-32.

Zueva, O.S., 2016. Structure and properties of aqueous dispersions of sodium dodecyl sulfate with carbon nanotubes. Russ. Chem. Bull., 65: 1208-1215.

Zueva, O.S., V.V. Salnikov, Y.N. Osin and Y.F. Zuev, 2016. Influence of carbon nanotubes on surfactants supramolecular structures. Liq. Cryst. Their Appl., 16: 90-96.

Zueva, O.S., Y.N. Osin, V.V. Salnikov and Y.F. Zuev, 2014. Research of carbon nanotubes suspensions: The emergence of mesoscopic structures from the self-assembly of surfactant molecules. Fundam. Res., 11: 1021-1027.

Zvereva, E.R., O.S. Zueva and R.V. Khabibullina, 2016a. The influence on the rheological quality of liquid fuel oil by nano-additives, including carbon nanotubes. Chem. Techol. Fuels Oils, 52: 1-6.

Zvereva, E.R., G.R. Mingaleeva, R.V. Khabibullina and G.R. Akhmetvalieva, 2016b. Improvement in the viscosity characteristics of boiler oil by additives. Pet. Chem., 56: 65-67.