Development of the composition of depressor - dispersant additives for petroleum fuels

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Abstract. The most appropriate and cost-effective way to improve the low temperature properties of petroleum fuels is addition of depressor and dispersant additives (DDA). The purpose of research was to develop the compositions of the depressor and dispersant additives for modified petroleum fuels preparation. To achieve the objectives it was necessary to formulate the steps of the research aimed primarily at solution of major questions and problems in the development of the depressor-dispersant additives compositions for petroleum fuels. As a result of performed studies, the composition of the depressor-dispersant additives for petroleum fuels was found. Based on the characteristics of structure and properties of many polymers, synthetic rubbers of polyolefin type – linear olefin copolymers – they should be related to the most promising for modification of fuels. To improve the temperature limit of filterability and sedimentation stability it was necessary to reduce particle size and molecular weight of polymers by the process of thermal degradation. The analysis of the resulting degradants was performed using the Geppler viscometer to gain dynamic viscosity data. Based on the studies a schematic diagram of the preparation of modified oil fuels was developed, resulting in the compounding and manufacturing technology of the depressor and dispersant additives that can comprehensively affect the low temperature properties of petroleum fuels.
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Introduction

Rational use of oil lubricants, improving their quality and resources expansion are the main tasks of modern refining and petrochemical industries (Kemalov *et al.*, 2013; Kayukova *et al.*, 2013; Kemalov and Kemalov, 2013). The problem of improving the low temperature properties of fuels and lubricants is important and urgent (as cold climate zone in Russia takes in more than 80 % of the country). The problem is dramatized by the fact that an increasing proportion of oil produced in Russia is of paraffinic type, i.e. containing a significant amount of alkanes with normal or low-branched structures. The latter differ from other petroleum hydrocarbons by the increased pour point temperature, which leads to degraded low-temperature properties of both the oil and refined products. There is a number of ways to improve the low temperature properties of petroleum fuels (Akhmetov, 2002):

• Reduction of the fraction boiling end for 40-60 °C, i.e. removing high melting paraffin hydrocarbons therefrom;

• Using the processes of urea, zeolite and microbiological dewaxing, i.e. decrease in the total content of paraffinic hydrocarbons;

• Use of hydrocracking, hydroisomerization, catalytic dewaxing, allowing to convert paraffinic hydrocarbons into hydrocarbons of other classes, to crack or isomerize them;

• Blending fuels with waxy products;

• Use of depressants (Popova, *et al.,* 1995; Jianglu *et al.,* 2001; Li, *et al.,* 2002; Bhattacharyya, *et al.*, 2003; Hancsók, *et al.*, 2008; Zhang, B., 2008; Beck, *et al.*, 2009; Carter and Green, 2010; Maithufi, *et al.*, 2011; Misra, and Murthy, 2011; Waynick, 2011; Ravi and Subramanian, 2013; Zak, *et al.,* 2014).

The most appropriate and cost-effective way to improve the low temperature properties of petroleum fuels is addition of depressor and dispersant additives (DDA). The purpose of research was to develop the compositions of DDA for the preparation of modified petroleum fuels. To achieve the objectives it is necessary to formulate the steps of the research aimed primarily at solution of major questions and problems in the development of DDA compositions for petroleum fuels:

1. Analysis of the state of current scientific and technical developments and application prospects of the DDA aimed to improve low temperature properties of petroleum-based fuels;

2. Physicochemical analysis of the original and the modified fuels;

3. The choice of components for the composite polymer base of DDA and the conditions and methods of combining them;

4. The research of destruction process with the involvement of developed composite polymer

systems to improve efficiency of DDA and the sedimentation stability of modified fuels;

5. The comprehensive analysis of the degradation products using standard and instrumental methods of analysis.

Based on the characteristics of structure and properties of many polymers, synthetic rubbers of polyolefin type – linear olefin copolymers (LOC) – should be related to the most promising for fuels modification ones. When modifying fuels the main challenge is to find the rational ways to combine fuels with additives. During direct injection of LOC into the fuel we failed to achieve complete dissolution of the former, despite the fact that the mixing process was carried out at temperatures up to 50 ºC.

Method

It is known (Kayukova *et al.*, 2013, Kemalov and Kemalov, 2013; Kemalov *et al.*, 2013), that low-molecular compounds have molecular weight (MW) of 500, compounds with MW of 500-5000 are oligomers, compounds with a molecular weight over 5000 – are high-molecular compounds (HMC). Similar to low molecular weight compounds (LMC) polymer cannot be dissolved in any solvent. Evidently, ether both low molecular weight compounds and polymers have a physico-chemical mutual affinity or not. In the first case, a true solution forms, in the second – a colloidal solution. Polymer solutions - are thermodynamically stable homogeneous molecular-dispersed mixtures of high and low molecular weight compounds. As is known, the solubility of the polymer depends on the chemical structure of its chains, the nature of the solvent and temperature.

In this paper, linear olefin oligomers (LOO-330), polyolefins (PO-340), spatial olefins (SO-185), distillate oil absorbent (DOA-140) were selected as the LMC for dissolving high molecular compounds.

The analysis of modified diesel and marine fuels is an important step in assessing the choice of composite-polymer base (CPB) components and the conditions of alignment. One of the main indicators of low-temperature properties of fuel is pour point, so the next stage of research was to study the dependence of the pour point on the type and the quantity of CPB. The low-temperature properties of fuel were determined according to the methodic of Russian Standard (GOST 20287-91 “Petroleum. Methods for determining the fluidity and solidification temperature”).

Analysis and results

It was found that the modification of fuels using inherently numerous petrochemicals virtually has no effect on the rate of the cloud point (change by 1-2 °C), which is confirmed by data in the literature (Kemalov *et al.*, 2013; Kemalov and Kemalov, 2013; Awaja and Pavel, 2006; Zhang, B., 2008). Thus, the most effective were the samples when their concentration in the diesel fuel is 0.07 wt. % and over. The samples of diesel fuel containing indicated amount of CPB solidified at minus 46 °C, i.e. the exponent of the depression reaches 30 °C. With further increase in the concentration of these samples the freezing temperature increased by 3-4 °C. We assume that that was due to the fact that molecules of our samples, where the n-paraffins were enclosed, started to aggregate, which reduced the mobility of the phases, and therefore the freezing temperature rose. The developed CPBs were similarly injected into the marine fuels. It was found out that the most effective were the fuels containing 0.07 and 0.09 wt. % of CPB. In the case of marine fuels pour point reduced to minus 43 °C, i.e. maximum depression was 30 °C.

Fuel, modified with the developed CPB, had acceptable indicators of freezing temperature values. To improve such operational indicators as critical filterability temperature (CFT) and sedimentation stability it was necessary to reduce the particle size of CPB as well as the values of molecular weight of the polymer, which would cause an increase in the reactivity of both the polymer dispersion of CPB and complex structural units and aggregative combinations of modified fuels [8, 9]. In order to reduce the molecular weight it was necessary to conduct thermal decomposition of obtained CPB. The obtained samples of destructurized LOC had the following physico-mechanical properties: the average molecular weight - 6400-18500 cu; density - up to 875 kg/m^3.

For the comparative analysis the degradation products were dosed into the original diesel fuel in equal amounts of 0.07 wt. %. LOC destruction products were much more efficient as depressants than the original polymers. The original LOC rubbers lowered the freezing temperature of the fuel for 18-20°C, a critical filterability temperature - for 7-8 °C, while the products of their degradation reduced these figures much more efficiently: the freezing temperature - for 21-27 °C and the critical filterability temperature - for 9-13 °C, depending on the depth of degradation.

The influence of the molecular weight of degradants and the degradation temperature on the low-temperature properties of the modified diesel fuel (DF) was studied. Degradants samples D-18-3 and D-18-7 with the MM of 8300 and 10100 cu, respectively, had the optimal depressant activity. At MM values below 8300 cu the depressant activity of degradant reduced. Perhaps this was due to the fact that the decrease in the values of these indicators was followed by the increase of degradants unsaturation that could

lead to unwanted polymerization and polycondensation reactions, i.e. the formation of new unwanted structures and polymer fragments.

Fig. 1 shows the curve of the dependence of the depression indicator from the additive concentration in the fuel that has an extreme nature with a peaking at 27 °C at a concentration of 0.07 wt. % .

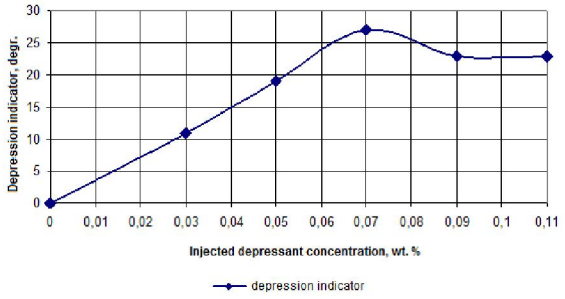

Fig. 1. The dependence of depression indicator of the modified diesel fuel from the injected additive concentration

Discussion

Our modified diesel fuel met the requirements of TU 38.101889-81 for DZp (TU – The Russian standard "Technical conditions", DZp – the Russian mark of winter diesel fuel with additives) for its performance indicators.

The next stage of the received degradants analysis was to determine their dynamic viscosity using the Geppler viscometer with falling ball. The data obtained was used to calculate the dynamic viscosity (Fig. 2).

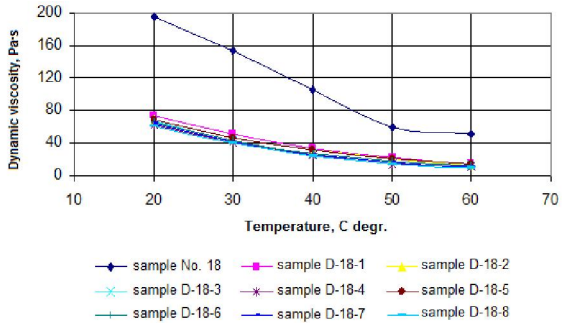

Fig. 2. The dependence of dynamic viscosity from the measurements temperature for sample number 18 and its degradants

As can be seen from Figure 2, degradants had much lower viscosity compared to the original polymer solution, indicating a decrease in the molecular weight of polymer and the effect of the degradation process. As the temperature increased, the viscosity of degradant reduced.

Next, the results of the structural-dynamic analysis of the modified diesel fuels by NMR spectroscopy are shown.

Using the experimental data obtained in studies by NMR relaxometry (Bayer, *et al.*, 2010; Berman, *et al.*, 2013; Charlier, *et al.*, 2013; Conte and Alonzo, 2013), with the use of our methodology, we calculated thermodynamic parameters of the modified DF with the sample of additive D-18-7.

For spin-spin and spin-lattice interaction activation energies for different temperature ranges were calculated. The activation energies for the spin-lattice interaction for the fuel containing 0.03 and 0.11 wt. % of a sample are shown in Fig. 3a.

Based on the obtained experimental data, one of the most important thermodynamic parameters of the system – an indicator of the change in entropy of the system S was calculated using the method of viscous flow activation thermodynamics calculation (Fig. 3b).

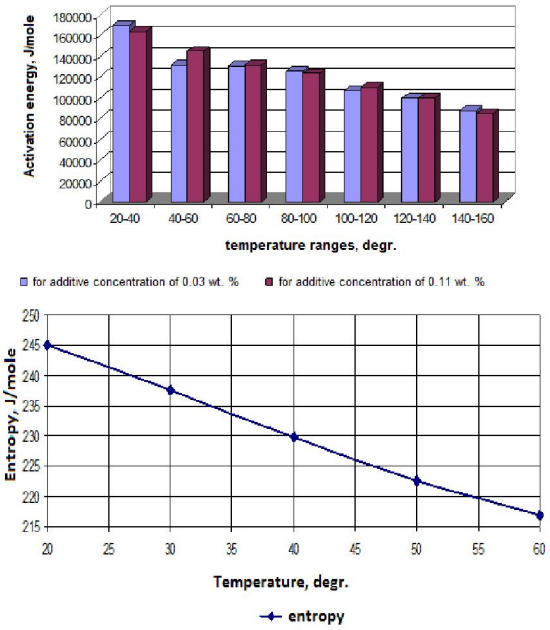

Fig. 3. Thermodynamic characteristics: a - the values of activation energy changes for the spin-lattice interaction for modified DF with the additives concentrations of 0.03 and 0.11 wt. %; b - the dependence of the values of entropy change from the measurement temperature

Figure 3b shows that with the increase in measurement temperature entropy of the system decreased, apparently, due to the structuring of modified fuel, therefore the degree of order of the system increased.

Summary

Based on the studies a schematic diagram of the preparation of modified oil fuels was developed, resulting in the compounding and manufacturing technology of the depressor and dispersant additives that can comprehensively affect the low temperature properties of petroleum fuels.

To improve the temperature limit of filterability and sedimentation stability it was necessary to reduce particle size and molecular weight of polymers by the process of thermal degradation. The analysis of the resulting degradants was performed using the Geppler viscometer to gain dynamic viscosity data.

The most effective were the samples when their concentration in the diesel fuel is 0.07 wt. % and over. The developed CPBs were similarly injected into the marine fuels. It was found out that the most effective were the fuels containing 0.07 and 0.09 wt. % of CPB. In the case of marine fuels pour point reduced to minus 43 °C, i.e. maximum depression was 30 °C.

The results presented above are of great value for the petroleum refining industry in general and for Russia in particular. As mentioned above, it became possible to improve the quality of the diesel fuel so that it can be used in winter conditions. But still remains the problem connected to a high pour point of the fuels we dealt with during the present research. To further improve the quality of the fuels it is necessary to conduct more research work aimed to develop complex multifunctional additives able to improve the freezing temperature values, critical filterability temperature, sedimentation stability as well as the pour point values.

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