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Obtaining Effective Depressor Dispersant Additives for Diesel Fuel Based on Pentaerythritol

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Abstract: In the development of a depressant additive for diesel fuels, unsaturated fatty acids with pentaerythritol, the characteristics of which correspond to TU 38.401.1059-97, were selected as the main component. The choice of pentaerythritol was due to the following reasons: firstly, unsaturated organic acids, which do not have a permanent consumer, are inexpensive products produced in the country, which are formed in industrial production.

Keywords: Diesel fuels, additive, depressant, component, pentaerythritol, oleic acid.

Introduction:

The quality of diesel fuel is closely related to the reliability and durability of the engine. The use of low-quality diesel fuel leads to poor performance of the high-pressure fuel pump, rough engine operation, increased carbon formation, reduced combustion efficiency, increased smoke emission, etc. One of the main disadvantages of diesel fuels is their physicochemical properties, which makes it difficult to start diesel engines in winter.

Pentaerythritol (PE) is a polyhydric alcohol containing 4 hydroxyl groups and a neopentane carbon skeleton. PE is widely used in the petrochemical industry. For example, fire-resistant heat-resistant compositions [1-3], alkyd varnishes, paints and resins [4,5], chemically resistant polymeric materials (pentaplast) [6], non-ionic surfactants [7], antimicrobial agents [8], stationary phases for chromatographic separation, polyoxidation inhibitors, [9], [10] agents [11].

The industrial method of producing PE is the aldol condensation of acetaldehyde with formaldehyde in an alkaline medium, followed by recrystallization [12], but, unfortunately, this process is associated with the formation of by-products that have low market demand and the high cost of removing them from commercial PE, therefore, modern technologies are constantly being developed [13-15].

Currently, the main producer of pentaerythritol in the Russian Federation is the Metafrax company; according to annual reports for 2018-2020. The stability of the PE market, as well as the expansion of production capacities, is noticeable. At the same time, there is a large share (~60%) of commercial products exported to foreign countries (Belgium, Germany, Italy, Korea, the Netherlands, Poland, Estonia, Belarus). According to the Ministry of Industry and Trade, the share of Russian pentaerythritol in the EU market is 40%[16].

Of the various products based on pentaerythritol, esters are of greatest interest. Among the wide range of applications of such compounds, their use as lubricants for special aviation equipment [17] and plasticizing compositions [18] deserves special attention.

There are a number of requirements for industrial plasticizers arising from technical and economic points of view: low volatility, absence of odor and color, chemical inertness, low cost, environmental safety, and compatibility with the polymer material [19].

According to the requirements, mainly pentaerythritol esters and linear or branched acids with an average molecular weight of 400-800 g/mol are used as plasticizers [20,21]. Currently, these compounds are gradually replacing the traditionally used phthalate plasticizers, the production of which cannot fully meet the increasing environmental requirements [22, 23]. For example, in European countries and the USA, the use of phthalate plasticizers such as DBP (benzylbutyl phthalate) in children's products has been permanently banned since 2005 [24].

Of great interest are esters of pentaerythritol and branched acids, which, due to their isomeric structure and high molecular weight, provide low diffusion, i.e., they have a higher resistance to emissions from the polymer compared to plasticizers with a linear structure [25].

The use of pentaerythritol esters as lubricants is closely related to the development of aircraft gas turbine engines. As aircraft designs become more complex, the requirements for lubricating oils under extreme operating conditions have also become more stringent, such as thermal and thermal-oxidative stability, compatibility with various additives, good lubricating properties and viscosity index. From an environmental point of view, ester oils are preferable, since base oils produced from petroleum sources are not renewable and difficult to biodegrade. According to statistics, when disposed of or leaked, most lubricants (50-60%) come into direct contact with soil, water and air, posing a potential threat to the ecosystem [26]. Standard mineral oil cannot fully meet these high performance standards, so synthetic ester oils almost completely dominate this market segment.

Mixed esters of pentaerythritol are used as lubricants, for example, the composition of 36/1 K and 36/1Ku-A oils is known, which contain products obtained by esterification of PE with a mixture of C5-C9 synthetic fatty acids, with the addition of paraoxyphenylamine (antioxidant content) in the amount of 2% [27]. In addition, sterically hindered esters are used as heat carriers where fluidity is required at low temperatures, as well as lubricants in metal rolling. The high quality of the ester base has allowed foreign companies to organize the production of synthetic oils, plastic lubricants and hydraulic fluids for special equipment with improved performance characteristics [27]. The high technologies used in the creation of ester oils are constantly being improved and modernized, and therefore meet the requirements of environmental safety, resource conservation and diversification of areas of application. The low level of domestic production of synthetic lubricants is primarily due to the lack of synthetic raw materials, additives, and advanced scientific and technical capacity [28,29].

The traditional method for obtaining esters is the esterification reaction, which consists of the interaction of an alcohol with a carboxylic acid or its anhydride, catalyzed by Brønsted (HCl, H2SO4) or Lewis (AlCl3, ZrCl4, etc.) acids [30].

It is known that the etherification reaction is reversible, and when the process is carried out in the liquid phase, it occurs with a small thermal effect, and in the gas phase with an exothermic effect and high values of equilibrium constants [31]. The production of pentaerythritol esters has long been the focus of attention, as evidenced by numerous publications devoted to the products obtained by etherification of various individual carboxylic acids and their mixtures and transetherification of vegetable oils with neopolyols.

METHODS

The synthesis of depressant compounds is carried out by etherification. The reaction was carried out in three-necked flasks equipped with a stirrer and a thermometer. 10 g of pentaerythritol alcohol was placed in the flask, and 30% of the 1% orthophosphoric acid catalyst was dissolved in toluene solvent and 40 g of oleic acid were added to it until it was dissolved, based on the mass of pentaerythritol. The reaction mixture in the flask was heated to 100-1100 °C at atmospheric pressure for 4 hours with stirring. Then the reaction mixture was cooled to room temperature of 20-25 °C. After the reaction was completed, 8 g of 5% sodium hydroxide solution was used to neutralize the unreacted oleic acid. During the neutralization process, 5% sodium hydroxide solution was added to the ether part of the mixture until litmus paper turned blue. The resulting ester was separated from the lower aqueous layer in a Buchner funnel and filtered through porous filter paper. After filtration, the oleic acid ester PEO was formed, and the reaction yield was 42.29 g (84.58%).

As a result, it was found that complete conversion of pentaerythritol was observed when the molar ratio of alcohol to acid = 1: 4, therefore, this molar ratio was used later. It was found that orthophosphoric acid significantly accelerates the process compared to the thermal option of process control, however, the use of catalysis with inorganic acids helps to accelerate undesirable negative osmolization reactions of the reaction mixture, negatively affects the color of the product, and also increases the complexity of the subsequent stages of separation.

In all synthesis options, complete separation of the water of reaction was observed. Carrying out the synthesis at high temperatures (in the absence of a solvent) leads to a decrease in the yield of tetraesters, which leads to the formation of by-products (which worsen the color indicators - a necessary parameter characterizing the quality), which are not completely removed from the target product. A similar result was observed when using homogeneous catalysts. At the same time, the thermal etherification option in solvent conditions shows the best results.

Thus, for further studies, the following parameters were used: the amount of azeotrope-forming substances toluene 30% of the reaction mass; catalyst 1%; pentaerythritol ratio: acid = 1: 4 (mol.); reaction zone temperature 100-110 0C. After removing the water released as a result of the azeotropic reaction with the solvent, the remaining solvent was removed by distillation at atmospheric pressure, and then excess acid was removed under vacuum.

The introduction of the extractant into the crude product was carried out by stirring for 2 hours (ratio 1-1, 1-2) at 500C; no transesterification and hydrolysis were observed. The resulting mixture was stored at -300C for 10-12 hours. After the formation of two phases, the etherification product was separated from the extractor by decantation. The extractor residues were removed by vacuum drying for 2-3 hours. When regenerating the extractor, it was possible to reduce the loss of the target product to 5-7%.

The recrystallization method was used to purify the crystalline products. Methanol was used in 5 to 15 (wt.) relative to the extracted product. Except for pentaerythritol tetraolein, acetonitrile was used in 4-5 times excess (wt.) for its extraction. The recrystallization temperature was -300C, the time for tetraolein was 1.5 hours, for the rest 10-12 hours.

The implemented methods of separation and purification turned out to be very effective, and due to the high quality of the target product, the thermal etherification option in the presence of a solvent is preferred.

Low-temperature properties are characterized by the cloud point, the filtration limit temperature and the freezing point. The cloud point is the temperature at which the phase composition of the fuel changes, since a solid phase appears along with the liquid phase. In this case, the fuel loses its transparency and becomes cloudy due to the release of microscopic ice crystals (if there is water in the fuel) and mainly solid hydrocarbons. However, when cloudy, the fluidity of the fuel does not change. The size of the crystals is such that they pass through the filters. At the maximum filtration temperature, the crystal size of the solid hydrocarbons increases and they do not pass through the filters, i.e. the fluidity of the fuel deteriorates. At the crystallization point, the crystal lattice hardens so much that the fuel loses its fluidity.

First trial: During cooling, the sample is continuously stirred with a stirrer for 20 s and rested for 15 s. When the thermometer shows a temperature close to the expected cloud point, the test tube is removed from the cryostat and compared to the standard sample to observe the turbidity. If the fuel is not cloudy compared to the transparent standard, the test tube is lowered back into the cryostat. With each subsequent decrease in the temperature of the sample by 1 0C, it is taken for comparison with the standard. When a visible turbidity appears in the sample that does not disappear with stirring, the temperature is recorded. The temperature at which the appearance of turbidity in the tested fuel is observed is taken as the cloud point of this fuel sample. This method determines the cloud point of diesel fuels without additives and tests with the addition of various amounts of additives.

Second trial: Constant stirring is maintained at the same interval with a difference of 15-170C between the sample and the coolant residue. 50C before the expected freezing temperature, the sample is removed from the cryostat and tilted at an angle of 45° for 1 minute. If the sample is mobile, it is lowered back into the cryostat, then every 10C the sample temperature is lowered and tilted at an angle of 45°. When the sample is completely stationary at an angle of 45° for one minute, the operation is stopped and the temperature is recorded as the freezing point of the sample.

Filtration limit temperature (on a cold filter) - the highest temperature at which a certain volume of fuel does not flow from a standard filter unit for a certain time during cooling under standardized conditions.

Third trial: The measuring vessel is filled to the marked mark with the sample and an insulating ring is placed on the bottom of the sleeve. The vessel is closed with a suitable stopper with a filter pipette and a thermometer. After installation in the apparatus, the lower part of the filter is placed at the bottom of the measuring vessel, parallel to the thermometer pipette and 1.5-2 mm above the bottom of the vessel. The body is placed vertically in a cooling bath 85 mm deep, in which the temperature is maintained at -34 °C. A vacuum device is connected to the pipette using flexible hoses connected to a tap, then a vacuum is applied and the air flow is adjusted. Given that the cloud point of the samples under study is known, the determination begins when the sample is cooled to 5 °C above the cloud point. After setting the required temperature, it is necessary to turn on the valve to connect the filter to the vacuum, which simultaneously turns on the stopwatch and causes the sample to be sucked into the pipette through the filtration mesh. After the fuel reaches the mark on the pipette, the tap is returned to its original position, so that the sample is poured into the measuring vessel and the stopwatch is stopped. If the fuel consumption time does not exceed 60 seconds, the temperature is further reduced in 1°C increments. The temperature at which the sample stops flowing through the filter or the pipette does not reach the mark within 60 seconds is considered the maximum filtration temperature for that sample.

RESULTS

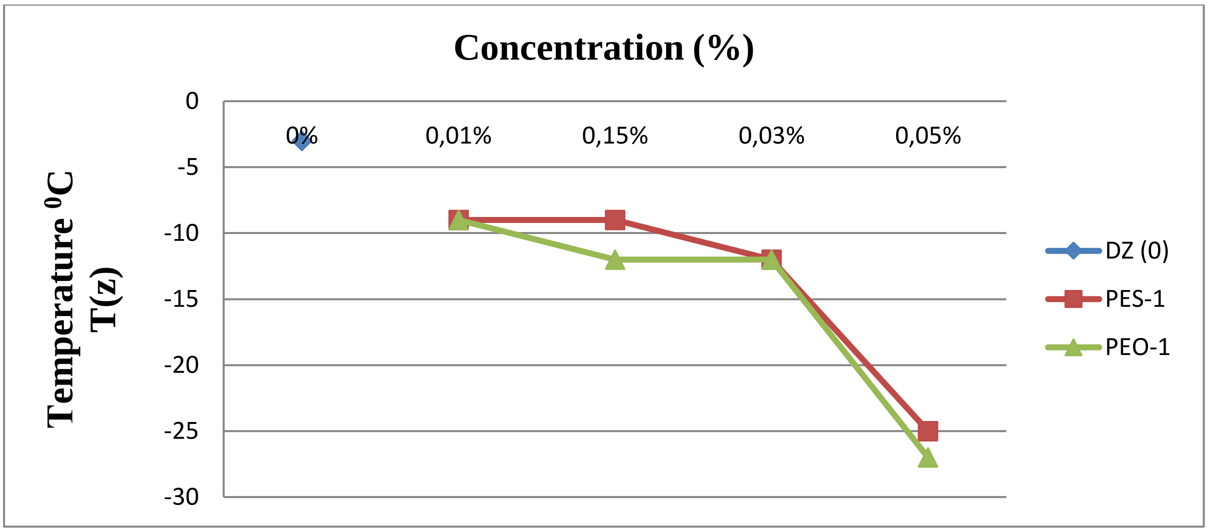
Taking into account the analysis of the literature data, it should be noted that homogeneous and heterogeneous catalysts (sulfuric acid, orthophosphoric acid, sulfonic cation exchangers, etc.) are widely used, but, unfortunately, the use of catalysts negatively affects the purity of the product, as a result of which it becomes difficult to obtain the desired tetrasubstituted pentaerythritol esters, which worsen the properties (color, viscosity, etc.). Thus, to avoid the above, we used the option of thermal etherification of pentaerythritol (self-catalysis).

The dynamics of changes in the cloud point, freezing point and filter limit temperatures are presented in Figures 1-3.

The dependence of the degree of change in the low-temperature properties of diesel fuels on the amount of added additives and the relationship between the hydrocarbon composition of the fuel and the efficiency of adding this additive are shown.

The dependence of the cloud point on the amount of additives added is shown in Figure 1.

Figure 1. CHANGE IN FREEZING TEMPERATURE BY ADDING DEPRESSOR ADDITIVES TO ECO DIESEL FUEL



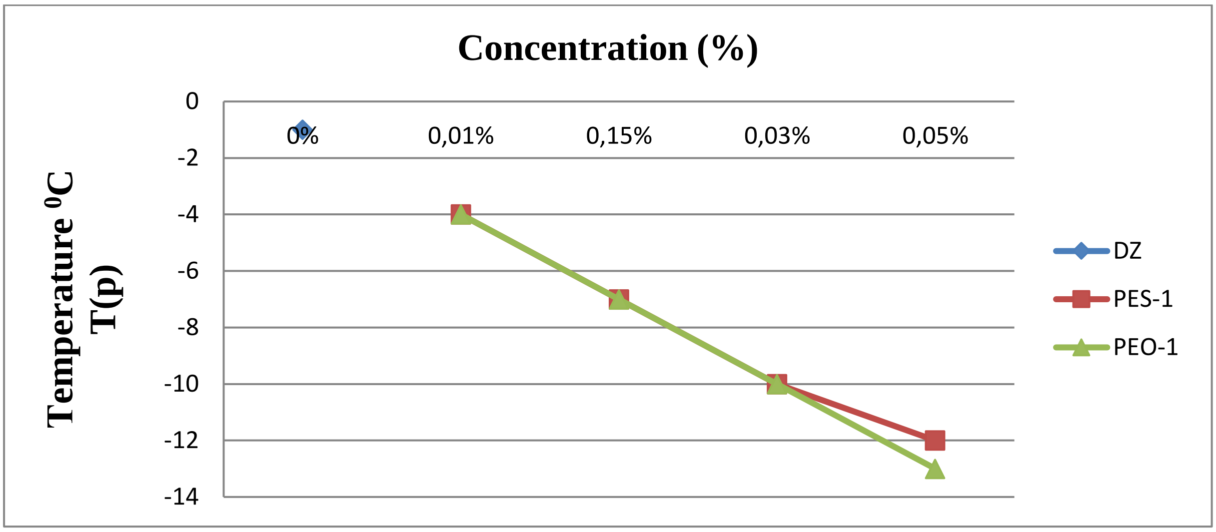
PEO - limit temperature of clouding ability of the sample;

PES - limit temperature of clouding ability of the sample;

DZ - limit temperature of clouding ability of the sample.

The dynamics of changes in the freezing and filtration limit temperatures are presented in Figures 2-3. The dependence of the degree of change in the low-temperature properties of diesel fuels on the amount of added additives and the relationship between the hydrocarbon composition of the fuel and the efficiency of adding this additive are shown. The dependence of the freezing point on the amount of added additives is shown in Figure 2.

Figure 2. CHANGE IN CLOUD POINT BY ADDING DEPRESSOR ADDITIVES TO ECO DIESEL FUEL



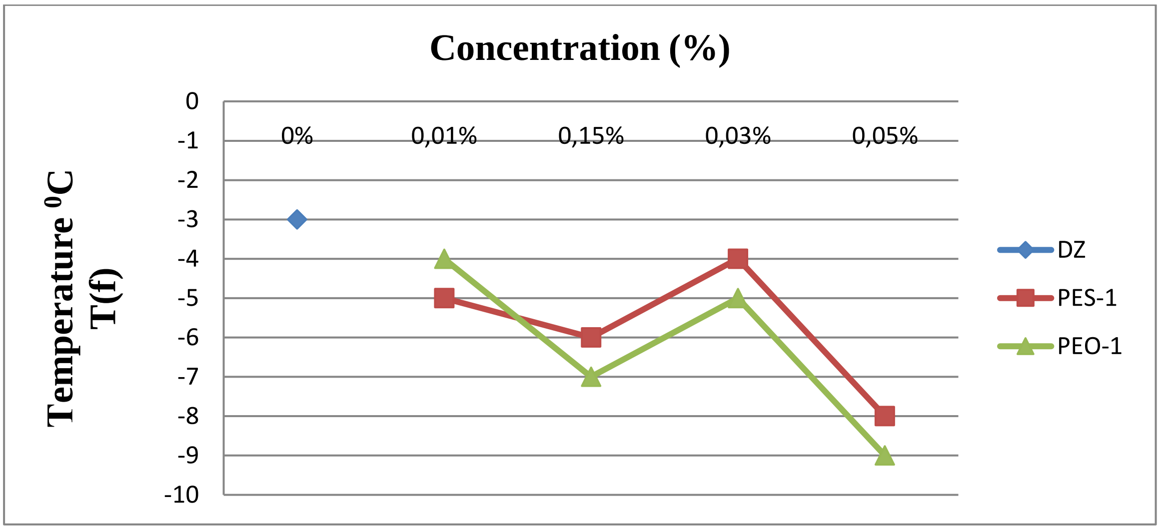
PEO - freezing point of the sample;
PES - freezing point of the sample;
DZ - freezing point of the sample.

Analyzing the obtained data, we can say that the depressant additive had the greatest effect on reducing the freezing point in samples 1 and 2. The freezing point of the PEO sample decreased from -9°C to -27°C. The greatest modification effect was achieved with an additive amount of 0.50% of the fuel volume. The freezing point of the PES sample decreased from -9°C to -25°C, which indicates the best compatibility of diesel fuel with the additive we have chosen. According to the modified low-temperature performance, PEO diesel fuel can be transferred from the category of summer grades of diesel fuel (freezing point -25°C) to the winter category (-27°C in temperate climates). The highest improvement in the freezing point was achieved with 0.5% of the additive added to the sample.

For sample DZ, this additive had no apparent effect on the freezing point shift.

The dependence of the maximum filtration temperature on the concentration of added depressant is given below.

Figure 3. CHANGE IN FILTERING TEMPERATURE BY ADDING DEPRESSOR ADDITIVES TO ECO DIESEL FUEL



PEO - the limit temperature of the filterability of the sample;
PES - the limit temperature of the filterability of the sample;
DZ - the limit temperature of the filterability of the sample.

Analyzing the obtained data, we can say that the depressor additive had the greatest effect on reducing the maximum filterability temperature in PEO - samples. The filterability limit temperature for the PEO sample decreased from -5°C to -9°C. The greatest modification effect was achieved with an additive amount of 0.5% of the fuel volume.

Based on the obtained data, it was concluded that the addition of the additive reduces the cloud point, freezing point and filterability limit temperature for both PEO and PES - samples. However, the PEO - sample showed the greatest sensitivity to the modification of low-temperature properties by the additive we selected. The freezing point decreased by 56.6%, the maximum filterability temperature decreased by 78%. It gives the highest rates of improvement of low-temperature properties for these samples.

Based on the data from the original PEO, PSO sample, after adding 0.2% mass, a decrease in low-temperature properties was observed with a certain amount of additives. It should be noted that the cloud point did not change significantly, as did the crystallization point and the final filterability. The optimal additive concentration to achieve the greatest effect of improving low-temperature properties was 0.5% of the diesel fuel sample. In conclusion, it can be said that the PEO depressant additive had the greatest effect on reducing the cloud point, freezing point and filter limit temperature of the diesel fuel sample.

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