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Synthesis Of Copolymers Based On Alkylmetacrylates And Their Influence On Low Temperature Properties Of Diesel Fuels

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Annotation: The article was prepared on the conducted test of the effect of additives synthesized by alkyl methacrylate on the low-temperature property of diesel fuel. The effect of the synthesized additives on n-paraffins in diesel fuel has been studied. The results of the study showed that both synthesized depressant-dispersant additives had a strong inhibitory effect on diesel fuel, while the threshold filtration temperature of 0.1% diesel fuel was reduced from -7 to -18, and the pour point - from -14. up to -28.

Keywords: Winter diesel fuel, hydrotreated diesel fuel, limiting filtration temperature, depressant, alkyl methacrylate's, fatty alcohols, styrene, BNKIZ, spectroscopy.

Introduction:

Rational use of fuels and lubricants, improving their quality and expanding resources are the main tasks of modern oil refining and petrochemical industry.

It is known that the main contributors to air pollution are vehicles, boilers and thermal power plants, industrial enterprises, ie all facilities that use petroleum products: diesel and furnace fuels, fuel oil,etc.[1]

Particular attention is paid to the reduction of toxic emissions into the atmosphere due to the constant increase in diesel fuel consumption. This task is a priority for the Republic of Uzbekistan and for all industrialized countries.Currently, an important solution to this problem is to strengthen the requirements for quality indicators of commercial diesel fuel. In the modern economy, along with improving product quality and environmental safety, continuous improvement of production efficiency is one of the pressing issues. [2]

In the production of diesel fuel at oil refineries, in addition to operational characteristics, special attention is paid to improving environmental performance. The most important operational characteristics of internal combustion engines are reliability, fuel efficiency and environmental safety, which depend on a set of design and operational factors, while fuel quality is one of the most important factors.The physicochemical properties of the fuel are the formation of a mixture in the diesel cylinders and the combustion processes, complete combustion of the fuel, fuel efficiency, the content of harmful substances in the engine exhaust gases, the fuel supply equipment resource and the required properties of the diesel fuel. [3]

The production and use of domestic fuels uses a variety of methods to solve problems that arise during the operation of diesel engines, such as improving the design of engines, one of the promising ways to improve their quality using additive compositions and additives that improve various properties.

With the help of add-ons it is possible to successfully solve a number of other important, cold freezing and complex problems of fuel production and use, reducing fuel consumption in engines, increasing their combustion completeness, reducing flue gas emissions.[4]

One of the current problems is the refining of oil and the supply of petroleum products, improving their quality and environmental safety during storage. The environmental properties of the fuel play an important role not only in the total amount of sulfur, but also in its low-temperature properties. However, the

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radical solution to the problem cannot be solved without the use of add-ons, which is the most advanced, economical and efficient way to obtain high quality fuel. Taking into account the above, Eugene Spala, Willem Van Dam Fuel carbide depressurizer, Wai Yin Leung Internal combustion, high-efficiency additives for diesel and jet engines, Simin Burigess, Jacqueline Mulqueen Additives for Improving Diesel Fuel Composition for High Pressure Fuel Systems, Mathieu Arondel, Thomas Dubois, Laurent Germanaud, Helene Rodeschini Additives for Improving the Decomposition Stability of Diesel and Biodiesel Fuels [5,6,7], Tyumen State University of Oil and Gas S.G. Agaev, A.M. Glazunov Production of depressurizers for diesel fuel on the basis of polycondensation reaction, North-East Russian Federal University named after M.K. Ammosov E.L. Iovleva Low temperature obtaining improved diesel fuels at the Russian State University of Oil and Gas named after I.M. Gubkin, T.N. Mitusova, A.M. Danilov, R.A. Terteryan, V.M. Kapustin, S.T. Bashkatova, I.N.Grishina, N.Sh.Mukhtorov, E.A.Burov, E.V.Kashin, E.N.Kabanova, Yu.B.Egorkina Numerous studies have been conducted on the production of winter diesel fuel, synthesis of additives that improve the properties of diesel fuel at low temperatures, technology, their theoretical and experimental basis, the impact of different multifunctional additives on diesel fuels with different hydrocarbon content and their mechanisms.[8]

In Uzbekistan S.M.Turobjonov, A.T.Jalilov, V.N.Hamidov, Sh.M. Saidakhmedov, G.R.Normetova, M.P.Yunusov, S.A.Abdurakhimov, O.M.Yoriev, As a result of scientific work of Yodgorov, O.S.Maxumova, B.A. Mukhamedgaliev, S.F.Fozilov and others, significant scientific and practical achievements have been made in the field of petrochemistry, oil and gas refining technology.[9]

The synthesis and use of depressant additives for various petroleum products, especially diesel fuel and oils, dates back to 1931, when synthetic additives for oils, paraflou, were obtained.[10]Industrial production of depressor additives for diesel fuel began in the mid-60s of the twentieth century. Depressor additives have been found during studies to significantly reduce the solidification and filtration limit temperatures of diesel fuel and to have almost no effect on its turbidity temperature. That is, this temperature has long been a key criterion in determining the suitability of fuel for winter use [11,12].

In the study of the synthesis of depressor additives, the synthesis of depressant additives began to develop rapidly only after it was determined that indicators such as fuel solidification temperature and leakage and absorption temperature, filtration temperature limit were crucial, not turbidity temperature.
Approximately 1960-1970, only 10 patents were obtained for depressant additives for diesel fuel, and more than 100 for 1970-1985 [21]. Most of the patents (approximately 90%) used polymer and copolymer compounds as depressant additives, including ethylene and propylene copolymers with various monomers. In addition, the main part of them are copolymers of ethylene and vinyl acetate.

The following compounds are used as depressor-dispersing additives for diesel fuel based on the analysis of the literature. Currently, depressor additives can be classified according to the chemical nature of diesel fuel as follows:

-ethylene copolymers with polyethylene macromolecules or polar monomers retained by the polar functional group (ethylene-vinyl acetate copolymers and their compositions, copolymers of ethylene with different polar monomers) [13,14,15,16];

-polyacrylates, polyalkylmethacrylate additives (polyalkyl- (met) acrylates, copolymers of alkyl (met) acrylates); [17,18,19];

-macromolecular ethylene-propylene, ethylene-propylene-diene and their decomposition products, copolymers of α-olefins, modified polyolefins [20,21,22];

- macromolecular poly-2,5-furandions [23,24,25];

- copolymers of fumaric acid and vinyl acetate macromolecules [26,27].

-arren polymers consisting of two or three monomers;

-non-polymeric chemicals (alkyl naphthalene; esters of polyhydric alcohols and high fatty acids [28,29,30].

It is known that the hydrocarbons that affect the low-temperature properties of diesel fuel are n-alkanes of simple structure with a large number of carbon atoms in this chain. To improve the low-temperature properties of diesel fractions, n-paraffin concentration reduction or depressor-dispersing

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additives are used. [31] The inclusion of depressant additives in the composition of DF allows to increase the range of its use in cold climates.

Currently, alkyl methacrylate-based additives differ from other types of additives in that the reaction is carried out in a normal atmosphere and at temperatures below 100 ^oC, as well as does not require complex technology. Based on the identified problems and gaps, the research goals and objectives are as follows. It consists of obtaining complex esters based on methacrylic acid and high-fat alcohols and studying the effect of bonding copolymers with styrene on the properties of diesel fuel at low temperatures.

Materials and methods:

Synthesis of alkyl (met) acrylates. The reaction was carried out in a three-nozzle flask equipped with a stirrer and a thermometer. The flask was filled with 14.4 g of methacrylic acid and 27.4 g of synthetic fatty alcohol of fraction C_8-C_{10} in a 1:1 ratio. While the mixture was slowly heated, 2.5 ml of 80% sulfuric acid was added dropwise. The reaction mixture in the flask was heated to atmospheric pressure at 80 ^0C for 3 hour and stirred. The reaction mixture was then cooled to room temperature to 20-25 ^0C. After the end of the reaction, a concentrated solution of sodium carbonate was used to neutralize the unreacted acrylic acid in the composition. During the neutralization process, a concentrated solution of sodium carbonate was added to the ether portion of the mixture while slowly stirring the liquid with a glass rod until the blue litmus paper was reddened. As a result of the release of carbon dioxide gas in the mixture, foam was formed in the mixture. The resulting ether was separated from the lower water layer using a Buchner funnel and filtered through a porous filter paper. After filtration, a complex ester of 37,202 g of acrylic acid was formed, the reaction yield was 89,0 %.

Copolymerization reactions of alkyl (met) acrylate and styrene. The copolymerization of the monomers being investigated by determining the dynamics of the change in the composition of the copolymers was carried out by aeration in glass ampoules at a temperature of 70^0C. The total concentration of monomers in solution ranged from 0.8 to 6.4 mmol/g. Initiator (DAC) concentrations ranged from 0.3 to 2.5% mol. Benzene, toluene and DMFA were used as solvents. Based on these results, the average compositions of copolymers obtained in different conversions of somonomers were calculated. For the copolymerization of a number of synthesized alkyl methacrylates and styrene, the content was determined by the IR spectrophotometer method depending on the ratio of the signals of the carbonyl groups (homopolymer spectra were used to identify the signals). When the copolymerization reached a certain conversion of monomers (in the range of 15–45%), the resulting reaction mass was diluted with benzene and the polymer was precipitated in isopropyl alcohol. The polymers were then dried under vacuum (20 ^0C) to a constant mass. Isopropyl alcohol was used as a precipitate in the form of copolymers of alkyl methacrylates and styrene.

Results: The structure of the copolymers was tested on an IR Shimadzu IRAffinity-1S-spectroscopic device.

Comparison of the IR spectra of the DMA-ST copolymer with the DMA monomer can clearly see the absorption frequencies specific to the fragments contained in the copolymer in the IR spectrum of the copolymer. The absorption field 1166.93 cm^{-1} is subject to CH_3-C-bond oscillations, 1456.26 cm^{-1} to alkyl group CH_2 oscillations, 1734 cm^{-1} is the valence oscillation frequency of the carbonyl group in the ester group and has a very strong intensity. 2866.22 cm^{-1} belongs to CH_3 and 2958.80 cm^{-1} belongs to CH_3 valence oscillations. It should be noted that the frequency of 1640-1660 cm^{-1} observed in the monomer spectrum does not occur in the IR spectrum of the copolymer. This frequency is related to the valence oscillation of the vinyl group C = C (Fig.1).

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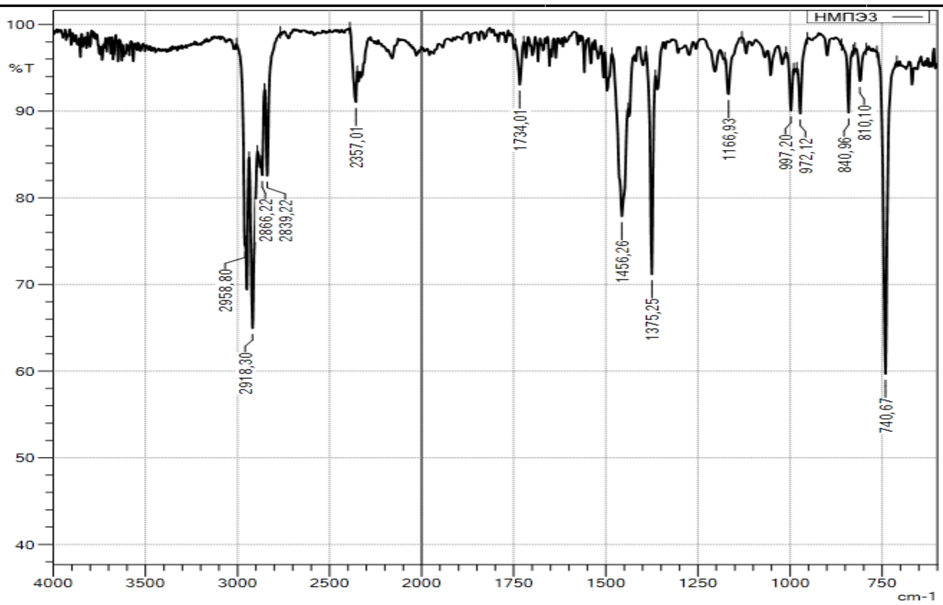


figure -1. IR spectrum of DMA-ST copolymer.

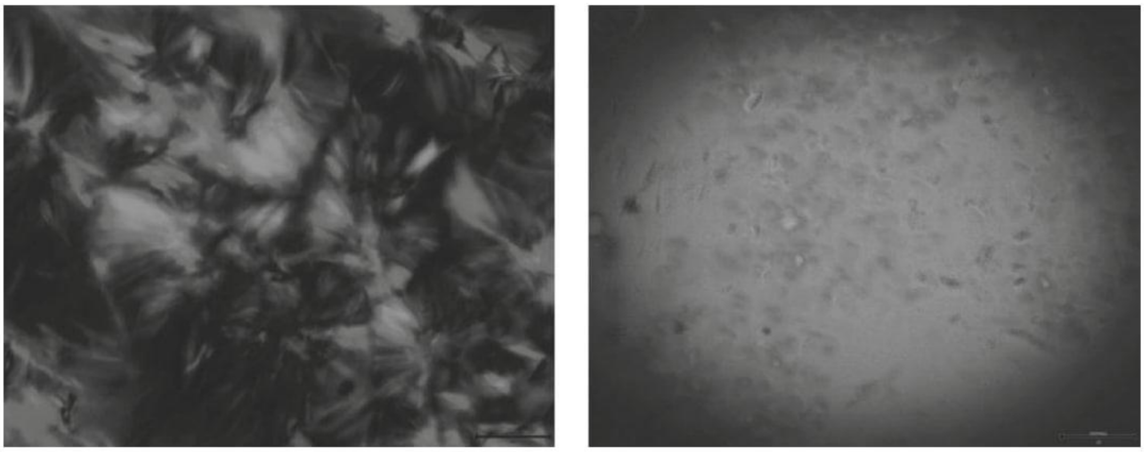
The C=C valence oscillation frequencies in the styrene aromatic ring appear in almost the same field as the aromatic valence oscillation frequencies in the monomer molecule. In addition, the IR spectrum of the copolymer shows 2 intense frequencies in the range of 700–800 cm^{-1}, which are also present in the styrene spectrum. This is due to the out-of-plane deformation oscillations of 5 CH groups in the aromatic ring of the compound, and intensive frequencies were observed in the area of 1000-1259 cm^{-1}, these frequencies are also present in the monomer spectrum, which is the frequency characteristic of the valence oscillation of the C-O-CO- of the garden in a compound.

To study the mechanism of action of synthesized additives on diesel fuel. The components of diesel fuel n-paraffins are determined according to the standard using the optical survey method. Paraffin crystal morphology was observed using a BX41-P OLYMPUS polarizing microscope. The samples were first heated to 50 ° C and then cooled to 10 ° C for 5 min. A small amount of paraffin was loaded onto a glass plate with a crystal central glass copper step. During the measurement, the temperature of the copper phase was controlled in a circulating bath at 10 °C (Fig. 2).

The mechanism of action of depressors is related to the effect of their paraffins on the crystallization process. A specific structural feature of copolymer macromolecules (modifiers of paraffin crystals) is a mixture of long-line saturated hydrocarbon chains and polar functional groups or branched hydrocarbon fragments.

Figure 2

a) without additive DF **b) additive DF**



Appearance of DF paraffin crystal morphology using BX41-P OLYPUS polarizing microscope.

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Due to the structural similarity of the paraffins and linearly saturated fragments, which appear on the microscope, the coordination of the additive macromolecules was observed on the surface of the paraffin crystal nuclei. Further growth of paraffin crystals is inhibited by the presence of polar groups or branched joints of macromolecules. As a result, the crystallization of paraffin begins at a lower temperature or continues through the formation of fine aggregates consisting of a stable crystalline modification of paraffin. The crystallization of paraffins in the form of the most stable crystalline phase greatly prevents the adhesion of the crystals formed in the mesophase during the crystallization of the kerosene fraction.

To study the effect of synthesized additives on the properties of diesel fuel at low temperatures. In conducting experiments for this study, we used diesel fuel from Bukhara Oil Refinery LLC without hydrotreated additives. The effect of the synthesized additives at different concentrations (0.1-0.5%) on their properties at low temperatures when added to hydrotreated diesel fuels produced at the Bukhara Oil Refinery (Table 1).

Table 1

Diesel fuel of synthesized additiveseffect on the properties of low temperatures

№	**The name of the sample**	**Additional, mas.%**	**Blurring temperature, ^{0}C**	**Freezing temperature, ^{0}C**	**Poir pount temperature, ^{0}C**
1	**Winter diesel fuel norm**	-	minus 5	minus 25	minus 15
2	**Diesel fuel without additives**	-	minus 4	minus 14	minus 7
3	**№1 addtivel**	0,1	minus 5	minus 21	minus 17
		0,5	minus 5	minus 25	minus 23
4	**№1 additive**	0,1	minus 5	minus 27	minus 18
		0,5	minus 5	minus 28	minus 19

As can be seen from the table, positive results were obtained when different amounts (0.1-0.5 mas.%) Were added from the synthesized additives to the limit temperature values of solidification and filtration of diesel fuel taken as a sample. When tested in the laboratory under Bukhara Oil Refinery laboratory, the maximum solidification temperature is increased to 7 ^{0}C with the addition of 0.1% to diesel fuel from № 1, the maximum filtration temperature is added to 12 ^{0}C, the maximum solidification temperature is added to 15 ^{0}C with the addition of 0.5%, the minimum filtration temperature is 18 ^{0}C. When 0.1% is added to diesel fuel, the maximum solidification temperature is reduced to 13 ^{0}C, the low filtration temperature is reduced to 13 ^{0}C, and when 0.5% is added, the high solidification temperature is reduced to 14 ^{0}C, and the low filtration temperature is reduced to 14 ^{0}C.

The results of the above test showed positive results in terms of the limit temperature of solidification and filtration of diesel fuel when 0.1-0.5% of the synthesized additives were added to the diesel fuel.

Conclusion:

The main purpose of the study was the synthesis of alkyl methacrylates and styrene-based additives that improve the low-temperature properties of diesel fuel. When the effect of the synthesized additives diesel fuel on n-paraffin hydrocarbons was studied, adsorption of long alkyl chains in the copolymer on the surface of n-paraffins was observed, and the polar functional groups prevent crystal formation, ie fusion with each other. Based on the results of experimental tests, we can see that the additives have a positive effect on the properties of diesel fuels at low temperatures.

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