**Effect of Lubricating Additives Derived from High-Paraffin Industrial Waste on the Kinematic Viscosity of Diesel Fuel**

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**Abstract:** Higher paraffins isolated from secondary by-products can be oxidized to higher fatty acids, followed by modification of their methyl esters with safflower oil, enabling their application as an import-substituting lubricating additive that improves the viscosity of diesel fuels. To select an optimal formulation compatible with diesel fuel, esters and safflower oil were blended in various ratios, and five different diesel fuel blend samples containing the lubricating additive were prepared to evaluate stable and uniform dispersion in the diesel fuel medium. The viscosity dynamics were determined using an LOIP LT-910 viscometer in accordance with the requirements of GOST 31391–2009.

**Keywords:** paraffins, oxidized, fatty acids, modification, fatty acid, an optimal formulation, safflower oil, lubricating additive, dispersion, viscosity dynamics.

**INTRODUCTION**

Among the various products derived from petroleum, diesel is the most commonly used fuel, and its utilization is growing continuously around the world due to the higher thermodynamic efficiency and fuel economy of diesel engines over the petrol counterparts. Shows that the global demand for diesel and gasoil (middle distillates) is expected to increase from 1660 billion liters in 2017 to 1834 billion liters in 2040 the statistical data released by OPEC [1].

In October 1996, Europe mandated a maximum limit of 0.05 wt % sulfur in diesel fuel.1 The Nordic countries had already taken similar action when in 1992 Sweden introduced Class with sulfur content less than 10 ppm by mass, and Class 2 type fuels with sulfur content 50 ppm by mass. Class 1 now accounts for nearly 100% of the Swedish diesel market. In Finland, a fuel known as City Diesel (50 ppm max sulfur) has over than 80% market share. Diesel fuel is now becoming more widely available in Germany, the United Kingdom, Denmark, and other European countries.

The introduction of low-sulfur diesel fuel has caused some problems due to the desulfurization process, which removes the natural lubricating properties of the fuel. Shortly after the launch of low sulfur diesel fuels in Sweden, the failure of the rotary fuel injection pumps increased dramatically. These pumps rely on the fuel for lubrication, and the failures were linked directly to the reduced lubricity of low sulfur fuels. Treating the fuel with suitable additives restored the fuel’s lubricity and eliminated pump failures.

Biodiesel is easily prepared from vegetable oil triglycerides through the transesterification reaction with methanol. Fatty acids comprise 94-96% of the whole mass of the triglyceride molecule and the beneficial ability of biodiesel on lubrication characteristics of lowsulfur diesel fuels could be attributed to the existence of these acids According to Bowden and Tabor, the addition of a small amount of fatty acid to a nonpolar mineral oil or to a pure hydrocarbon can bring about a considerable reduction in the friction and wear. Wei and Spikes observed that a significant wear reduction was produced by fatty acids, introduced into hydrotreated fuel at low concentration: caproic acid (100 ppm) and palmitic acid (300 ppm). A more recent paper discusses the effect of fatty acids (C6-C18) at low concentrations (50-750 ppm) in n-hexadecane on wear of steel under boundary lubrication conditions [2].

The lubricity of the diesel fuel can be improved by adding some chemical substances as additives. Arkoudeas et al. Mentioned that, the lubricity of number 1 diesel and number 2 diesel fuel appears to rise from very small quantities of polar, to quite high boiling point components. Agarwal et al. Described that, lubricity additives comprise a range of surface active chemicals. They have an affinity for metal surfaces and form boundary films that prevent metal – metal contact, which otherwise could have led to wear under light to moderate loads. When different additives are simultaneously present in a fuel, their surfactants can competitively react with the metal of friction surfaces. Surfactants of other additives can be sorbed on the friction surfaces, forming boundary layers capable of preventing the metal from reacting with the anti-wear additive. They have observed that the 1-amino glycerol mixed with diesel fuel as an additive gives less wear scars than that of glycerol compounds. Moreover, when the organic compounds are used as anti-wear additives, the polar parts are dissolved in the hydrocarbon fuels so that the polar/non-polar effects are balanced. As a result, the mixed compound is adhered on the rubbing metal surfaces in the form of boundary lubrication to reduce the wear [3].

Diesel fuel injection equipment relies on the lubricating properties of diesel fuel. A lack of lubricity in diesel fuel produces a shortened life of engine components, suchas diesel fuel injection pumps and injectors. Furthermore, to prevent surface-to-surface contact and reduce wear under loads, the fuel must have the ability to form a protective ﬁlm that is indicated by the ﬁlm percentage in a lubricity analysis [4].

An alternative diesel fuel that is steadily gaining attention and significance is biodiesel, which is defined as the monoalkyl esters of vegetable oils and animal fats. Previous literature states that low blend levels of biodiesel can restore lubricity to (ultra-)low-sulfur petroleum-derived diesel (petrodiesel) fuels, which have poor lubricity. This feature has been discussed as a major technical advantage of biodiesel. In this work, the lubricity of numerous fatty compounds was studied and compared to that of hydrocarbon compounds found in petrodiesel. The effects of blending compounds found in biodiesel on petrodiesel lubricity were also studied. Lubricity was determined using the high-frequency reciprocating rig (HFRR) test. Dibenzothiophene, which is contained in nondesulfurized petrodiesel, does not enhance petrodiesel lubricity. Fatty compounds possess better lubricity than hydrocarbons, because of their polarity-imparting O atoms. Neat free fatty acids, monoacylglycerols, and glycerol possess better lubricity than neat esters, because of their free OH groups. Lubricity improves somewhat with the chain length and the presence of double bonds. An order of oxygenated moieties enhancing lubricity (COOH > CHO > OH > COOCH3 > C=O > C-O-C) was obtained from studying various oxygenated C10 compounds. Results on neat C3 compounds with OH, NH2, and SH groups show that oxygen enhances lubricity more than nitrogen and sulfur. Adding commercial biodiesel improves lubricity of low-sulfur petrodiesel more than neat fatty esters, indicating that other biodiesel components cause lubricity enhancement at low biodiesel blend levels. Adding glycerol to a neat ester and then adding this mixture at low blend levels to low-lubricity petrodiesel did not improve petrodiesel lubricity. However, adding polar compounds such as free fatty acids or monoacylglycerols improves the lubricity of low-level blends of esters in low-lubricity petrodiesel. Thus, some species (free fatty acids, monoacylglycerols) considered contaminants resulting from biodiesel production are responsible for the lubricity of low-level blends of biodiesel in (ultra-)low-sulfur petrodiesel. Commercial biodiesel is required at a level of 1%-2% in low-lubricity petrodiesel, which exceeds the typical additive level, to attain the lubricity-imparting additive level of biodiesel contaminants in petrodiesel [5].

It is estimated that approximately 10% of global lubricating oil production (including esters) are fully synthetic products [6]. Specific properties of esters enable them to meet the vagaries of lubrication challenges posed by modern machines both technically and with respect to environmental protection. In comparison to hydrocarbon oils, esters exhibit strong dipole moments. This improves their lubricity by adhering strongly to the metal surface at the friction point. They also show excellent qualities as components of modern, environmentally friendly synthetic engine oils produced from saturated olefin oligomers C8-C12 (polyalphaolefins). Addition of esters enhances oil lubricity and enables them to form stable solutions with polar additives. A great majority of ester oils are physiologically harmless and easily biodegradable in the natural environment [7; 8]. The only barrier to the wide application of esters is their relatively high cost of production, 4-15 times higher than that of conventional mineral oils. Possibilities for applying compounds of unconventional structure, like complex esters, natural fatty acid derivatives as well as products of their chemical modification as lubricants are being considered [9]. New methods for synthesizing low waste and energy saving ester oils using advanced catalytic systems including enzymes are being designed [10].

Therefore, the development of a technology for producing highly efficient lubricating additives that substitute imports, based on the processing of secondary by-products, is of significant importance. One of such products is waste hexane, which is generated as a liquid secondary by-product during the polymerization process at the “Uz-Kor Gas Chemical” joint venture LLC.

Due to the current inability to convert waste hexane (spent hexane) into a value-added product, the development of technologies for its processing remains a pressing issue for researchers and specialists in the fields of chemistry, petrochemistry, and oil and gas processing [11].

The chemical composition of the processed hexane, obtained as a secondary product of the suspension polymerization process at Uz-Kor Gas Chemical JV LLC, consists predominantly of normal-and iso-chain saturated and naphthenic hydrocarbons, mainly forming the C8-C33 fraction. More than 88% of the processed hexane is composed of normal-chain alkanes such as octane, decane, dodecane, tridecane, tetradecane, hexadecane, heptadecane, and heptacosane [12].

It is well known that the paraffin oxidation process has extremely high practical significance in the organic and petrochemical synthesis industry.

It should be noted that the rate of hydrocarbon oxidation in the liquid phase depends on a number of factors, including catalyst concentration, temperature, and the partial pressure of oxygen (i.e., the rate of air transfer from the gas phase into the liquid phase). As a result of this process, synthetic fatty acids in the C10-C20 range are formed [13; 14]. Synthetic higher fatty acids and their esters serve as a basis for the synthesis of additives aimed at improving the lubricating properties of diesel fuels.

**METHODS**

The relative viscosity of the proposed lubricating additive was determined using an LOIP LT-910 viscometer in accordance with the requirements of GOST 31391-2009 (Figure 1). The viscometer is a U-shaped glass tube with one arm having a wider section. A capillary is connected to the narrow section, and the upper part of the capillary is formed as a bulb, the upper part of which is also narrow. The upper and lower parts of the bulb are marked with the letters A and B, respectively. A rubber tube was attached to the end of the bulb, and the viscometer was placed in a thermostatic bath.



**FIGURE 1.** LOIP LT-910 viscometer

To determine the relative kinematic viscosity (ν, mm2/s) of the lubricating additive under investigation, the flow time of a clean solvent through the viscometer capillary was first measured, and the value was calculated using the formula presented below.

*v=Ct*

where, C - is the viscometer constant, mm2/s, t - flow time, s.

**RESULTS AND DISCUSSION**

Higher paraffins obtained from secondary by-products can be oxidized to higher fatty acids, followed by modification of their methyl esters with safflower oil, enabling their application as an import-substituting lubricating additive that improves the kinematic viscosity and lubricity of diesel fuels.

To select an optimal formulation compatible with diesel fuel, esters and safflower oil were blended in various ratios, and five different diesel fuel blend samples containing the lubricating additive were prepared to evaluate their stable and uniform dispersion in the diesel fuel medium.

Analysis of the rheological properties of colloidal dispersion systems plays a crucial role in assessing their physicochemical stability. In this study, five samples were blended with diesel fuel at concentrations of 100, 200, and 300 ppm, and their kinematic viscosity was evaluated at 40 0C over a period ranging from 12 to 72 hours. The selected temperature enables assessment of rheological stability under various operating conditions.

Initially, the kinematic viscosity at 40 0C was analyzed at time intervals of 12, 24, 36, 48, 60, and 72 hours.

At a concentration of 300 ppm, a sharp decrease in viscosity was observed, which is associated with agglomeration of the dispersed phase, formation of large clusters, and intensification of sedimentation processes. These dynamic changes provide an important basis for evaluating the rheological performance of the system and determining the stability of the colloidal system. Furthermore, the obtained results serve as a basis for selecting the optimal concentration of the lubricating additive for diesel fuel.

Based on the data presented in Figure 3, the dynamic variation of kinematic viscosity over time was evaluated. At a concentration of 100 ppm, the viscosity did not undergo any significant change over the observed time period, indicating high aggregative and kinematic stability of the dispersion system, with sedimentation and agglomeration processes occurring at a minimal level. At a concentration of 200 ppm, the viscosity initially decreased slightly and then returned to an equilibrium state, suggesting that the system reached equilibrium as a result of the redistribution of dispersed particles within the medium and changes in interaction mechanisms. At a concentration of 300 ppm, a sharp decrease in viscosity was observed, which is associated with agglomeration of the dispersed phase, formation of clusters, and intensification of sedimentation processes. These dynamic changes allow for the evaluation of the rheological behavior of the system and provide insight into the stability of colloidal and dispersion systems. Furthermore, the obtained results serve as a basis for selecting the optimal concentration of the lubricating additive for diesel fuel.

Based on the data presented in Figure 4, the dynamic variation of kinematic viscosity over time for the diesel fuel blend containing Sample 3 is shown. At a concentration of 100 ppm, the viscosity was largely maintained, with only a very slight decrease observed, indicating high aggregative stability and long-term colloidal stability of the system. At a concentration of 200 ppm, the viscosity initially remained unchanged; however, after 36 hours, a decreasing trend became apparent, followed by the establishment of a new equilibrium. This behavior can be attributed to the redistribution of dispersed particles within the medium and the balancing of interparticle interaction forces. At a concentration of 300 ppm, a gradual decrease in viscosity was observed, which indicates intensified sedimentation processes resulting from agglomeration of the dispersed phase and the formation of larger clusters. These dynamic changes are essential for evaluating the rheological characteristics of the dispersion system and are useful for determining the optimal additive concentration intended for blending with diesel fuel.

Based on the data presented in Figure 5, a graph illustrating the dynamics of kinematic viscosity of the production diesel fuel blend containing Sample 4 was constructed. At a concentration of 100 ppm, the viscosity remained almost unchanged, with only a slight decrease observed after 48 hours. This behavior indicates high aggregative stability of the dispersion system and a uniform distribution of colloidal particles. At a concentration of 200 ppm, the viscosity remained constant for a certain period, followed by a decrease after 36 hours, which is associated with the gradual activation of sedimentation processes of the dispersed particles. At a concentration of 300 ppm, a continuous decrease in viscosity was observed, indicating particle coalescence in the dispersed phase, formation of large agglomerates, and intensification of sedimentation processes under the influence of gravitational forces. These trends provide essential information for the development of diesel fuel additives and for the evaluation of their rheological properties.

Figure 6 shows the kinematic viscosity dynamics of the diesel fuel blend containing Sample 5. At 100 ppm, the viscosity remained nearly constant, with only a slight decrease observed after 48 h, indicating high aggregative stability and uniform colloidal dispersion. At 200 ppm, the viscosity remained stable throughout the entire testing period. At 300 ppm, a slight decrease in viscosity after 48 h was observed, which can be attributed to agglomeration of the dispersed phase and enhanced sedimentation processes.

**CONCLUSION**

To enhance lubricity, the methyl ester of the obtained fatty acid was modified with safflower oil, and comparison with literature data confirmed that the modified ester formed a stable colloidal system in diesel fuel at the optimal ratio. Overall, the results indicate that a concentration of 200 ppm for Sample 5 is optimal, ensuring stable colloidal-rheological behavior of the diesel blend without significant changes in viscosity over time. This additive exhibits the highest thermo-rheological stability among the studied systems and is considered the most suitable option for long-term storage and operational use.

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