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Green oxygenated compounds as components of B10 fuel

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This work is aimed to investigate the possibility of using glycerol-based oxygenate compounds, as well as pine oil, dioxane and cyclopentanone, as components of B10 fuel blends. As seen in our results, the fuel blend of B10 with the phenyl-1,3-dioxan-5-ol and 2-phenyl-1,3-dioxolan-4-ylmethanol mixtures, cyclopentanone, dioxane and solketal have shown better properties in terms of viscosity, flash point, cloud and pour temperatures, oxidation stability and corrosion resistance compared to diesel and B10. Plausible antioxidant mechanisms for glycerol ketals are proposed.

Keywords: Biodiesel, Biofuel, Biomass, Oxyganated compound, Glycerol

Introduction

Environmental problems occurring worldwide like the global greenhouse effect, acid rains, ozone layer depletion, global sea level rise, etc. have become more acute in the last decade. To ensure the stability of the ecological balance, strict restrictions are imposed in industry, agriculture and any field of general human activity. Transportation is one of the main sources of environmental pollution, and cars account for most of it, followed by trains and airplanes. In addition to harming the environment, these pollutants also threaten human health, leading to the extinction of some populations[1-3].

To overcome these problems, biofuels have become a very relevant direction. Biofuels are safer and more environmentally friendly because they are synthesized from biomass, such as vegetable oils and agricultural waste. Thus, biofuels can be an alternative to traditional hydrocarbon fuels. The increasing use of bioethanol and biodiesel, derived from crops such as corn, sugarcane, and soybeans, reduces dependence on oil and gas while creating new opportunities for the agricultural and energy sectors[4-12].

Currently, the use of multifunctional additives (oxygenates) is considered very promising to improve the quality characteristics of synthesized biofuels. The use of oxygenate additives reduces the amount of harmful gases in the combustion process, so the combustion is complete and the fuel is used more efficiently. Studies show that using oxygenated components expands biofuel reserves, improves quality characteristics, and reduces the toxicity of combustion products[13-20].

Considering the above, the presented work is relevant in the search for alternative fuel sources and in studying the operational characteristics of the use of oxygenate additives.

Experimental Section

Materials and Methods

All the chemicals for the synthesis of imidazole sulfates were obtained from commercial sources (Aldrich) and used as received.

NMR experiments were performed on a BRUKER FT NMR spectrometer (UltraShieldTM Magnet) AVANCE 300 (300.130 MHz for ^{1}H and 75.468 MHz for ^{13}C) with a BVT 3200 variable temperature unit in 5 mm sample tubes using Bruker Standard software (TopSpin 3.1). The ^{1}H and ^{13}C chemical shifts were referenced to internal tetramethylsilane (TMS). NMR grade $CDCl_3$ was used for the analysis of diesel and biodiesel samples.

Preparation of Biodiesel

For the process, 0.69 g of KOH is dissolved in 37.5 mL of unheated methanol. After complete dissolution, 50 mL of oil was added to the mixture. The mixture was added to a heat-resistant chemical glass container. It was then heated to 60°C. The solution was then mixed in a flask with the help of a stirrer. The transesterification reaction continued for 6 h with continuous stirring. This produced methyl esters of the corresponding fatty acid, which was biodiesel (Fig. 1).

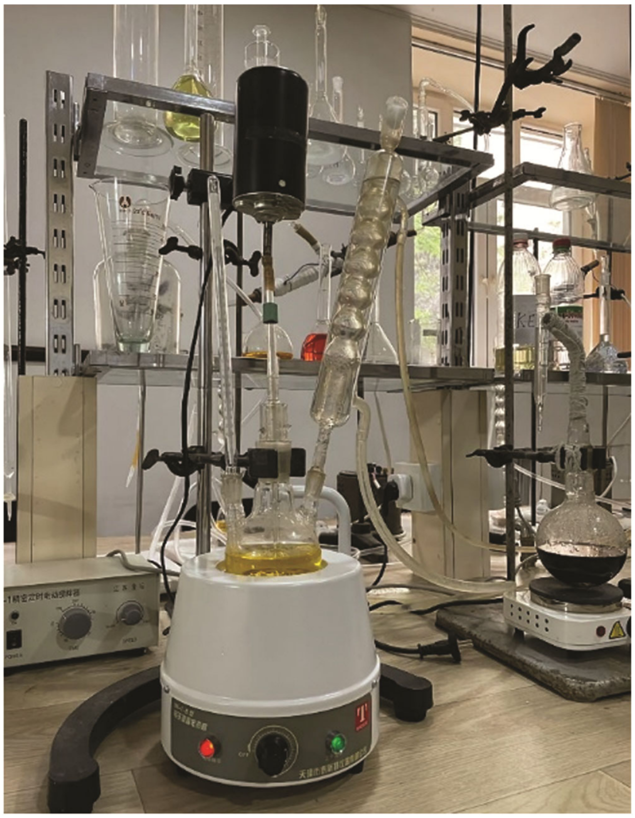


Fig. 1 — Set-up for the preparation of the biodiesel with ionic liquids

Preparation of B10 Biodiesel Fuel Blend

B10 biodiesel fuel was prepared by mixing volumetric amounts of diesel fuel and synthesized biodiesel fuel in a ratio of 90% :10%. The exploitation properties of the diesel, biodiesel, and B10 blends were determined according to ASTM standards.

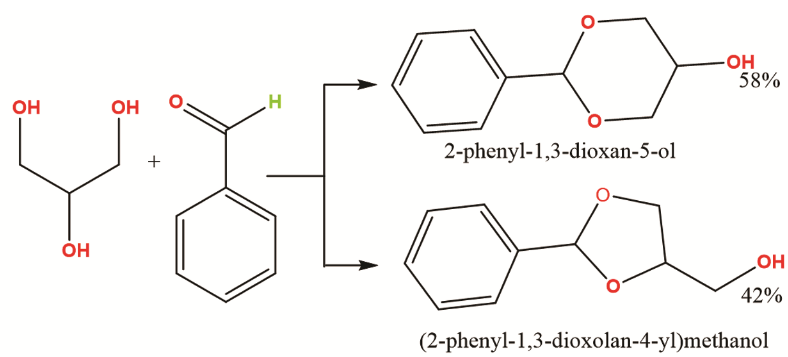
Preparation of oxygenates by condensation of glycerol and benzaldehyde (or acetone)

Glycerol oxygenate was obtained by the condensation reaction of glycerol and benzaldehyde in a solvent in the presence of a catalyst. Paratoluenesulfonic acid served as a catalyst, while benzene was used as a solvent. Condensation proceeds according to the reaction shown in Scheme 1:

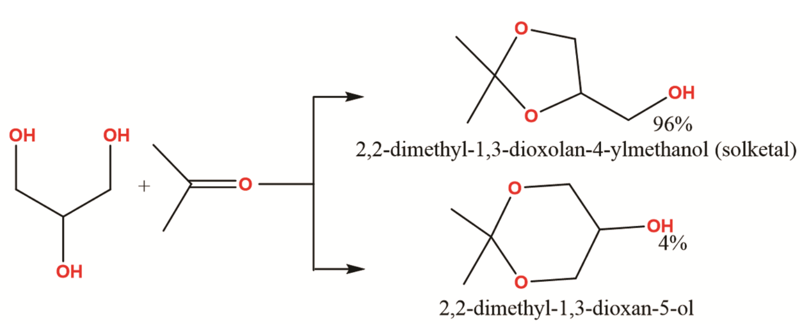
A mixture of 17.5 mL of glycerol, 19.2 mL of benzaldehyde, 25 mL of benzene and 1 g of PTSA acid catalyst was in a reflux 3-neck flask for 24 h. The synthesis was carried out by removing the water formed during the reaction with the Dean-Stark apparatus (Fig. 2). Condensation was carried out until the volume of water formed during the reaction was constant. By the same method, solketal was synthesized (Scheme 2).

Quantification of tar formed during the oxidation of the studied fuels

The apparatus shown in Fig. 3 was used to study the amount of tar formed as a result of oxidation in



Scheme 1



Scheme 2

Fig. 2 — Set-up for the preparation of the glycol acetal

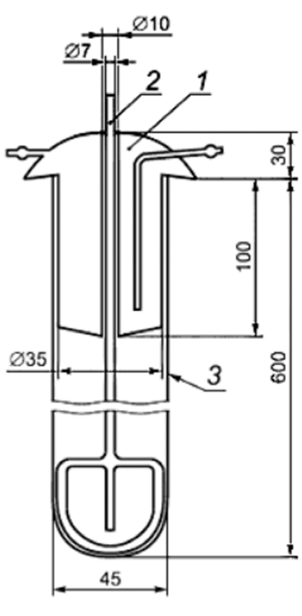


Fig. 3 — Apparatus for the oxidation of fuels

biodiesel fuels. An amount of 5 mL of the fuel used for the oxidation process was taken. The process was carried out at 90-100°C for 16 h (Fig. 3). The oxidation stability of fuel blends was controlled and estimated by the NMR method.

Results and Discussion

Today, one of the most important factors affecting the world economy and politics is oil and gas resources, which are the main sources of the planet's energy supply. Various sources have been developed to meet the need for energy. Therefore, more attention is paid to alternative energy sources, especially biofuels. Among biofuels, biodiesel is the most common one that meets environmental requirements. Biodiesel is an alternative energy source and can replace petroleum-based diesel fuel.

The urgency of biodiesel is due to its many advantages: it is ecologically safe, biodegrades very easily, increases the cetane number and the engine's operating time is extended. In addition, the by-product of biodiesel production is glycerol, which is used in many fields of science and industry.

In addition to this, there are conflicting aspects of biodiesel fuel according to its stability and freezing. For the increasing operation properties of biodiesel, it usually has to apply oxygenated compounds. The addition of oxygenated compounds to these mixtures as an additive can increase quality indicators.

Taking this into account, in the present work, oxygenates (total of 5% in B10) 2-phenyl-1,3-dioxan-5-ol (A) and 2-phenyl-1,3-dioxolan-4-ylmethanol (B) mixtures, pine oil (which consists of mainly cyclic terpene alcohols, known as alpha-terpineol ($C_{10}H_{18}O$) and alpha-pinene ($C_{10}H_{16}$), pure solketal, dioxane and cyclopentanone (structures are shown in Fig. 4) have been added to the B10 fuel blend to improve the quality.

The essential operational characteristics of fuel mixtures obtained after adding systems containing binary, ternary, and quaternary oxygenate components have been studied according to ASTM standards and compared with conventional diesel fuel.

As it is known from the literature, glycerol ketal, pine oil, ether oils, also oxygenated compounds can be used as fuel additives, which help to reduce particle emissions and improve the cold flow properties of liquid carrier fuels[17-20]. It reduces tar formation and improves oxidation stability. The operating characteristics obtained after adding two-, three-, and four-component oxygenates to B10 fuels are given in Table 1.

As seen from Table 1, the sulfur content, corrosion resistance characteristics, cloud and pour temperatures of the B10 fuel mixtures were superior compared to diesel and biodiesel. However, we want to focus specifically on the results obtained from the multicomponent systems. As seen from the obtained results, in multicomponent oxygenate systems, the essential parameter viscosity has sharply decreased compared to diesel and biodiesel. For example, the value of viscosity as a very important indicator for diesel engines was decreased up to 3.1 mm^2/s in the presence of the three-four oxygenated component systems B10 + (A+B) + cyclopentanone + dioxane and B10 + (A+B) + cyclopentanone + dioxane + solketal.

The flash point also has high significance for diesel engines. As demonstrated in our investigations, the best flash point (60°C) has the fuel mixture in the presence of the three-component system B10 + (A+B) + cyclopentanone + pine oil. The presence of oxygenated additives reduces the cloud and pour points of fuel mixtures. As seen, the best results are observed for the B10 fuel blends containing three and four-component oxygenates: for example, the cloud and pour point temperatures in the presence of four-component oxygenates (B10 + (A+B) + cyclopentanone + dioxane + solketal) were -21 and -29ºC, respectively. The obtained results show that the prepared fuel mixtures can be used in a wide operating range. This positively affects the fuel flow and atomization characteristics of the engine. Since oxygenate additives were added to B10 fuels by 5%, it did not have a serious impact on the cetane number (Table 1).

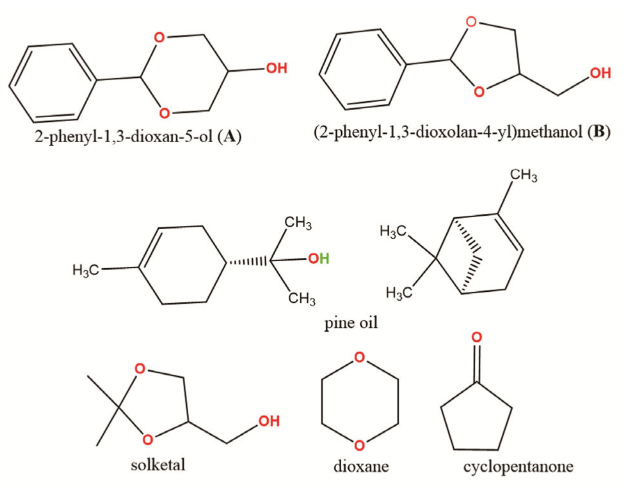


Fig. 4 — Structures of compounds added to B10 fuel

The density has slightly increased for all B10 fuel mixtures compared to diesel. However, since this increase is not significant, it has not negatively affected the operational characteristics.

The oxidation stability of B10 blends was tested by ASTM D 2274-03a and estimated by using NMR data. The oxidation stability of diesel and B10 blends before and after oxidation was estimated by the ratio of ^1H NMR integral intensity of the naphthenic-paraffinic region at 0.5-4.5 ppm to the sum integral intensity of the olefinic-aromatic region at 4.5-6.0 ppm and 6.6-9.0 ppm, accordingly (Table 2). If we compare the oxidation results, the best results were shown by the B10 + (A+B) +dioxane + cyclopentanone, B10 + (A+B) + solketal + cyclopentanone and B10 + (A+B) + cyclopentanone + dioxane + solketal fuel mixtures.

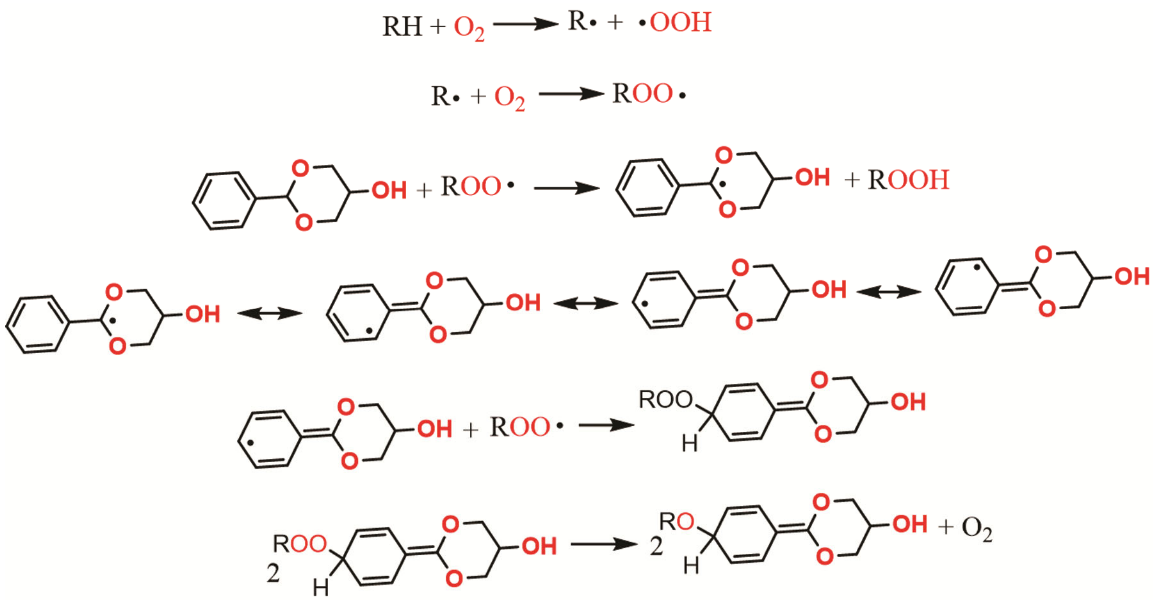
Plausible antioxidant mechanisms of investigated glycerol ketals are shown in Scheme 3.

Table 1 — Exploitation properties of diesel, B100, B10 and B10 fuel blends

Fuel blends	Viscosity at 20°C (mm^2/s)	Viscosity at 40°C (mm^2/s)	Relative density at 20°C (g/cm^3)	Flash point (°C)	Copper corrosion, 3 h at 50°C	Cloud point (°C)	Pour point (°C)	Sulfur (ppm)	Cetane number
Diesel	6,2	3,4	0,84	70	№2	+7	+0	50	43
Biodiesel	-	4,1	0,88	174	№1	+15	+8º	0	49
B10	5,3	3,3	0,85	120	№1	+6	-2	33	43.1
B10 + (A+B) +cyclopentanone	5.3	3.4	0.86	69	№1	-15	-22	33	41.7
B10 + (A+B) + cyclopentanone + solketal	5.2	3.2	0.86	70	№1	-19	-27	33	42.1
B10 + (A+B) + cyclopentanone + pine oil	5.3	3.3	0.86	60	№1	-18	-27	33	42.9
B10 + (A+B) + cyclopentanone + dioxane	4.9	3.1	0.86	73	№1	-19	-27	33	41.3
B10 + (A+B) + cyclopentanone + dioxane + solketal	4.9	3.1	0.85	70	№1	-21	-29	33	40.9
B10 + (A+B) + cyclopentanone + dioxane + pine oil	5.2	3.3	0.85	78	№1	-21	-27	33	41.1

Table 2 — Oxidation stability of diesel and B10 blends

	Diesel	B10 + (A+B) + CP	B10 + (A+B) + S	B10 + (A+B) + DO + CP	B10 + (A+B) + S + CP	B10 + (A+B) + PO + CP	B10 + (A+B) + DO + S + CP	B10 + (A+B) + DO + PO + CP
Before (OS_{NMR})	9.89	21.88	19.20	21.21	22.71	23.21	21.11	23.42
After (OS_{NMR})	5.88	54.88	32.00	20.37	23.51	34.12	20.97	32.27



Scheme 3

For other cases, we can also propose similar antioxidant mechanisms.

Conclusion

In the presented work, B10 fuel mixture, based on biodiesel from sunflower oil and methanol was prepared. The operating characteristics were compared with conventional diesel and it was determined that B10 was better quality. Also, 2-phenyl-1,3-dioxan-5-ol and 2-phenyl-1,3-dioxolan-4-ylmethanol mixtures, cyclopentanone, pine oil, and solk etal were added to the prepared B10 fuel series and examined. B10 + (A+B) + dioxane + cyclopentanone and B10 + (A+B) + dioxane + solketal + cyclopentanone fuels exhibited higher exploitation characteristics. We can especially note that the new types of fuel blends dominate the classic diesel fuel in terms of environmental and exploitation properties.

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