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Testing of Ethylene Glycol Ketal, Dioxane and Cyclopentanone as Components of B10, B20 Fuel Blends

Ibrahim Mamedov[a], Gular Mamedova[a], Nargiz Azimova[a]

[a]*Baku State University, Faculty of chemistry, Z. Khalilov 23, Baku, Azerbaijan*

ABSTRACT. The aim of the present work was to the preparation of biodiesel from sunflower oil and methanol by the transesterification reaction in the presence of the KOH. The conversion was 95% using a 1:3 molar ratio of oil to alcohol at 65°C. Important fuel physical properties of B10 and B20 fuel blends with (or without) oxygenated additivities by the ASTM standards had been investigated. Based on the obtained results is noted that the fuel blend B10 and B20 with oxygenated additivities has greater potential for diesel engines than, B100 and fossil diesel. The best result was demonstrated B10+1.4-dioxane fuel blend among the studied fuels.

Keywords: *transesterification, biofuel, biodiesel, ketal, oxygenated additivities*
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1. INTRODUCTION

Today one of the most important key factors to affect the world economy and politics is the petroleum and gas resources which are the main sources of world energy supply. In the modern world to meet the needs of energy different resources have been developed. But our planet has a lot of environmental problems with the exhaust toxic emission from the usage of fossil fuels. Another problem is the exhaustion of petroleum, natural gas, etc. resources. Therefore, alternative energy sources mostly biofuels are receiving more attention [1-4].

From the alternative type of fuels, biodiesel is a renewable resource consisting of fatty acid alkyl monoesters derived from vegetable oil, waste animal fats, or waste cooking oil. Important is need to note, at the combustion of biodiesel does not emit toxic substances that cause environmental problems due to the absence of aromatic, nitrogen and sulfur compounds [5-8].

In comparison with conventional diesel fuels, the oxygen in biodiesel may promote more complete combustion and thus reduce particulate matter, carbon monoxide and total hydrocarbons in ignition engines. According to a review of emission data for heavy-duty engines published by EPA (Environmental Protection Agency of USA 2002), from diesel to B20, carbon monoxide, toxic hydrocarbons and particle matters decreased by 13, 20 and 20 % respectively [9-11].

Considering the above, in the presented work, the transesterification reaction of sunflower oil with methanol in the presence of KOH was carried out. The important operational properties of B10 and B20 fuel blends on the basis of FAME were tested in the presence (or absence) of ethylene glycol ketal (EGK), 1.4-dioxane (DO) and cyclopentanone (CP). The oxidation properties of B10 and B20 fuel blends were estimated by using NMR data.

2. EXPERIMENTAL MATERIALS AND INSTRUMENTATION

All the chemicals for the synthesis of ethylene glycol ketal and dioxane were obtained from commercial sources (Aldrich) and used as received (Figure 1, 2).
Samples of diesel fuel, sunflower oil were purchased at a fuel station and markets in Baku, Azerbaijan. The B10 and B20 fuel blends with (or without) oxygenated additivities were prepared by mixing diesel and biodiesel.

NMR experiments have been performed on a BRUKER FT NMR spectrometer (UltraShieldTM Magnet) AVANCE 300 (300.130 MHz for 1H and 75.468 MHz for 13C) with a BVT 3200 variable temperature unit in 5 mm sample tubes using Bruker Standard software (TopSpin 3.1). The 1H and 13C chemical shifts were referenced to internal tetramethylsilane (TMS); the experimental parameters for 1H: digital resolution = 0.23 Hz, SWH = 7530 Hz, TD = 32 K, SI = 16 K, 900 pulse-length = 10 μs, PL1 = 3 dB, ns-= 1, ds= 0, d1 =1 s; for 13C: digital resolution = 0.27 Hz, SWH = 17985 Hz, TD = 64 K, SI = 32 K, 900 pulse-length = 9 μs, PL1 = 1.5 dB, ns= 100, ds= 2, d1= 3 s. NMR-grade CDCl3 was used for the analysis of ethylene glycol ketal and fuel blends.
The purity of the synthesized ethylene glycol ketal confirmed by thin-layer chromatography (TLC) on commercial aluminum-backed plates of silica gel (60 F254), iodine vapor was used as a visualizing agent, eluent- 5:2 hexane/ethyl acetate.

Corresponding author: bsu.nmrlab@gmail.com

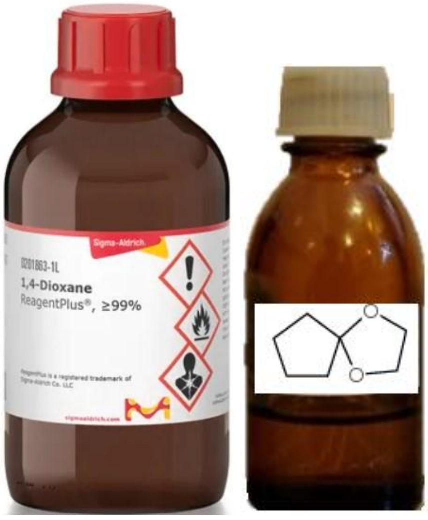

Figure 1. Dioxane and ethylene glycol ketal

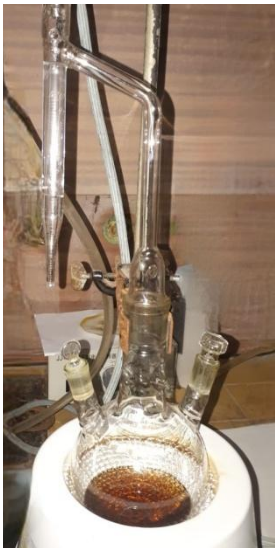

Figure 2. The preparation of the ethylene glycol ketal

The procedure for preparation of biodiesel

Sunflower biodiesel (B100) was obtained by dissolving 0.69 g KOH in 37.5 ml of methanol (CH3OH) without heating (at room temperature). After complete dissolution, 50 g of oil was added to this mixture. The reaction was carried out in a conical flask equipped with a reverse refrigerator and magnetic stirrer for 6 hours at 65 ºC (rotation speed was maintained at 1000 rpm). After stirring, the reaction mass was aged for at least 12 hours in a dividing funnel. The reaction mass was divided into 2 layers using a dividing funnel: the upper layer contained biodiesel, the lower layer-glycerine. Untreated biodiesel was repeatedly washed with water in order to remove catalysts. The conversion rate was 95% when using the molar ratio of oil to methanol 1:3 (Figure 3).

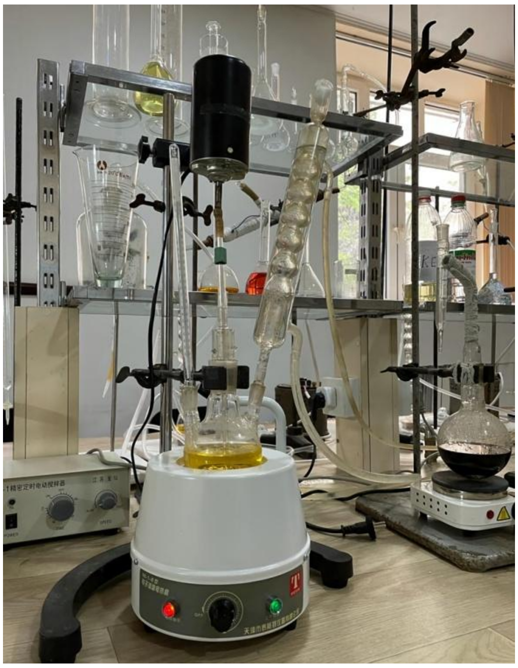

Figure 3. The preparation of the biodiesel

Figure 4. Biodiesel synthesized from sunflower oil and its blends were characterized in accordance with the American Standard of Testing and Materials (ASTM) methods.

The procedure for preparation of ethylene glycol ketal

A mixture of 30 g of pure ethylene glycol, 100 ml of cyclopentanone (in Figure 5), 0.75 g of p-toluene sulfonic acid (PTSA) was placed in a 500 ml conic flask fitted a reflux condenser and magnetic stirrer. The reaction mixture was stirred under 100°C for 5 working days. After the completion of the reaction mixture was neutralized with 0.5 g sodium acetate. In the next stage filtration and evaporation of the cyclopentanone had been carried out. The ketal was obtained by vacuum distillation, yield 65% (Figure 2).

Figure 5. Mixture of hydroxyl and cyclopentanone

3. RESULTS AND DISCUSSION

In our previous works [12-14], the preparation of methanol, ethanol biodiesels catalyzed by a new ionic liquid system (or KOH) and testing of their operational properties had been informed. This work is devoted to the preparation of methanol biodiesel from the sunflower oil, testing their different exploitation properties with (or without) the ETG, DO and CP additivities.

As known from the literature oxygenated compounds, such as glycerol ketals, pine oil (PO), essential oils, etc. can be used as a fuel additive to reduce particulate emission and to improve the cold flow properties of liquid transportation fuels. It helps to reduce gum formation, improves oxidation stability, etc. [15, 16].

The used feedstock sunflower physicochemical properties are shown in Table 1.

Table 1. Major fatty acids and physical properties of the refined sunflower oil

Fatty acid composition (wt.%)	16:0	18:0	18:1	18:2
	3.5–7.6	1.3–6.5	14–43	44–74
Acid value (mg of KOH/g)	0.28±0.5			
Saponification value (mg KOH/g)	193.3±0.5			
Iodine value (g I2 per 100 g)	121.4±0.5			
Viscosity (cP)	34.1±0.5			
Flash point (°C)	265			
Pour point (°C)	+12			
Density (g/cm3)	0.9186			

Considering the above indicated, the properties B10 and B20 blends in presence of EGK, DO and CP was studied. The physical properties of the diesel, sunflower biodiesel (B100), B10 and B20 blends with (or without) oxygenated additivities were investigated and the results are shown in Tables 2, 3.

Table 2. The physical properties of B10, B20, B100 and diesel fuels

Properties	ASTM Methods	ASTM diesel	ASTM biodiesel	diesel	B10	B20	B100
Relative density at 20°C, g/cm^3	D1298	0.8-0.84	0.86-0.9	0.837	0.848	0.855	0.88
Viscosity at 40°C, mm^2/s, min-max.	D445	2-5	3.5-5.0	3.44	3.54	3.60	4.1
Flash point, °C, min.	D93	65	>120	70	114	105	174
Cloud point (°C)	D2500	-12	<20	7	3	5	+12
Pour point (^{0}C)	D2500	-15	<15	0	-7	-5	+6
Iodine value g (l_2)/100 g	-	60-135	<120	1.58	44.5	45.7	110.5
Sulfur, ppm, max.	D 975-14	15	15	50	35	33	0
Water and sediment, vol%, max.	D 975-14	0.05	0.05	0	0	0	0
Copper corrosion, 3 hr at 50°C, max.	D 975-14	№3	№3	№2	№1	№1	№1
Cetane number, min.	D 975-14	40	47	43	43.7	44.1	48.5

As seen in Tables 2 and 3 density decreased for all B10 and B20 fuel blends. The density is a factor governing the quality of crude petroleum, it is an uncertain indication of petroleum product quality unless correlated with other properties. But, kinematic viscosity significantly decreases for all fuel blends in the presence of 5% oxygenated compounds in the blends. Minimal kinematic viscosity has the B10+DO fuel blend (3.13 mm^2/s). The significantly decreasing viscosity positively influences the flow and sprays characteristics in the engine [2, 4].

The flashpoints are decreased for the biodiesel blends than for pure biodiesel (B100). The best flashpoint was demonstrated B10+DO fuel blend with the 78°C. The cloud and pour points for fuel blends at the presence of oxygenated additivities were decreased. The best cloud and pour points were typical for the B10+DO blend.

The amount of sulfur significantly decreased as the percentage of biodiesel and oxygenated compounds in blends from 50 up to 33 ppm, which is very important for the environment and human health. As shown in our experimental results, water, sediment, also copper corrosion parameters are excellent [8].

The oxidation stability of diesel and B10 and B20 blends before and after oxidation was estimated by the ratio of NMR integral intensity of the naphthenic-paraffinic region at 0.5-4.5 ppm. to the olefinic-aromatic region at 4.5-6.0 ppm. and 6.6-9.0 ppm. accordingly (Table 4).

Table 4. The oxidation stability of diesel and B10 and B20 blends

	diesel	B10	B10	B20	B10	B20	B10	B20
		FAME	FAME+EGK (5%)	FAME+EGK (5%)	FAME+DO (5%)	FAME+DO (5%)	FAME+CP (5%)	FAME+CP (5%)
Before (OS_{NMR})	9.89	11.28	8.95	8.21	15.71	13.32	11.6	10.31
After (OS_{NMR})	5.88	5.31	6.59	5.41	8.39	7.59	6.15	5.78

As seen in Table 4, high oxidation stability has the B10+DO fuel blend. The oxidation stability of other oxygenated fuel blends also is more than that of diesel and B100 fuel blends during the oxidations at 16 hours, at 95°C. This is due to the fact that oxygenated additivities protect the fuel from oxidation.

Considering the above indicated, we note that the B10+DO fuel blend has low kinematic viscosity (3.13 mm2/s), flashpoints temperature (78°C), high oxidation stability and best exploitation properties demonstrated.

4. CONCLUSIONS

The properties of diesel, B10, B20, B100 fuel blends with (or without) oxygenated additivities were investigated on the ASTM (Figure 4) standards.

Obtained results have demonstrated improvements of the important physical properties- such as density, viscosity, amount of sulfur, copper corrosion, flash-, pour- and cloud points for B10, B20 fuel with oxygenated compounds.

Summarizing the obtained data, we can note that the fuel blends B10, B20 with oxygenated compounds have greater potential for diesel engines than pure biodiesel (B100) and commercial diesel fuel. The best result was demonstrated B10+DO fuel blend among the studied fuels.

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