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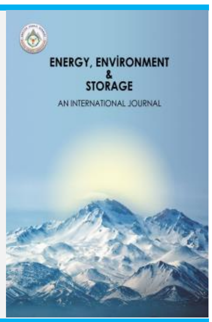

Testing of pine oil and glycerol ketal as components of B10 fuel blend

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ABSTRACT. The aim of the present work was to the preparation of biodiesel from sunflower oil and ethanol by the transesterification reaction in the presence of the KOH. The conversion was 88% at using a 1:3 molar ratio of oil to alcohol at 75°C. Important fuel physical properties of B10 blend with (or without) oxygenated additivities by the ASTM standards had been investigated. Based on the obtained results is noted that the fuel blend B10 with (or without) additivities has greater potentials for diesel engines than, B100 and fossil diesel.

Keywords: *: transesterification, biofuel, biodiesel, pine oil, ionic liquid*

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1. INTRODUCTION

Today there are serious environmental problems on Earth, such as the depletion of the ozone layer, the formation of acid rain, the accumulation of toxic chemicals in the upper atmosphere, the greenhouse effect and so on, which their formation have a significant role an automobile park of the world. Another problem is the exhaustion of petroleum, natural gas, etc. resources [1-4].

The development of new types of alternative biofuels sources is an actual problem of the modern world. Potential advantages of alternative biofuels for internal combustion engines are low emissions, longer engine life due to better lubrication, biological decomposition, high octane-cetane number, etc. In addition, biofuels do not emit toxic substances that cause environmental problems due to the absence of aromatic, nitrogen and sulfur compounds. One of the alternative types of fuel is biodiesel for diesel engines [5-8].

Alkaline catalytic systems are used in biodiesel industry, which leads to the formation of foam during cleaning, the formation of wastewater as a result of excessive washing. The choosing of the new catalytic systems is still relevant today in the production of biodiesel [9-12].

Besides indicated, the choosing of the new renewable raw materials sources also is a topical issue in the biodiesel industry [13].

2. MATERIALS AND METHODS

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

Samples of diesel fuel, sunflower and pine oil were purchased at a fuel station and markets in Baku, Azerbaijan. The B10 blends with (or without) oxygenated additivities were prepared by mixing diesel and biodiesel (Figure 1, 2).

NMR experiments have been 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); the experimental parameters for ^{1}H: digital resolution = 0.23 Hz, SWH = 7530 Hz, TD = 32 K, SI = 16 K, 90^0 pulse-length = 10 µs, PL1 = 3 dB, ns-= 1, ds= 0, d1 =1 s; for ^{13}C: digital resolution = 0.27 Hz, SWH = 17985 Hz, TD = 64 K, SI = 32 K, 90^0 pulse-length = 9 µs, PL1 = 1.5 dB, ns= 100, ds= 2, d1= 3 s. NMR-grade acetone-d_6 and $CDCl_3$ were used for the analysis of glycerol ketal and fuel blends.

The purity of the synthesized compounds was 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.

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Fig. 1. Pine oil and glycerol ketal

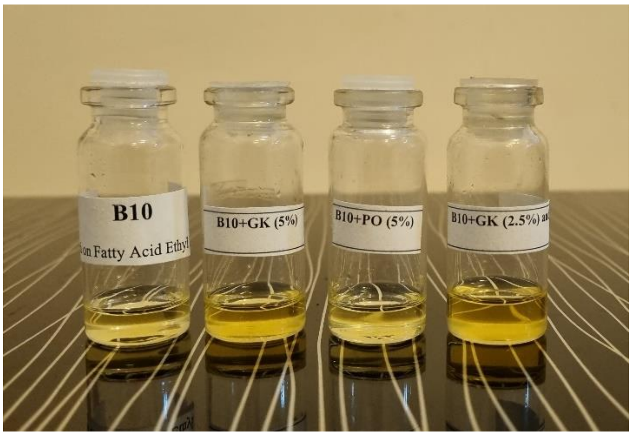


Fig. 2. The prepared fuel blends

2.1. The procedure for preparation of biodiesel

Sunflower biodiesel (B100) was obtained by dissolving 0.69 g KOH in 37.5 ml of ethanol (C_2H_5OH) 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 7 hours at 75 ºC (rotation speed was maintained at 1000 rpm). After stirring, the reaction mass was aged for at least 12 hours in 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 88% when using the molar ratio of oil to ethanol 1:3 (Figure 3).

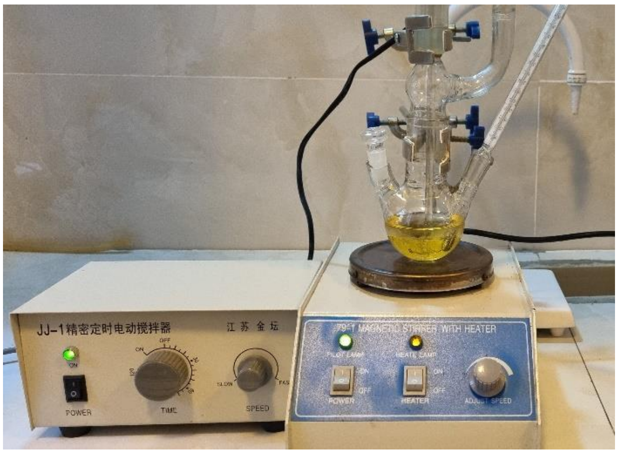
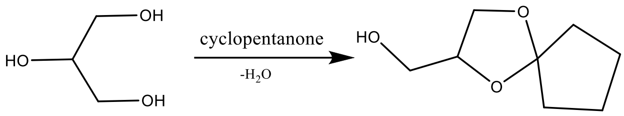


Fig. 3. The preparation of the biodiesel

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

2.2. The procedure for preparation of glycerol ketal (GK)

A mixture of 25 g of pure glycerol, 100 ml of cyclopentanone, 0.75 g of p-toluenesulfonic 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 acetone had been carried out. The ketal was obtained by vacuum distillation, yield 96%.



(96)%

3. RESULT AND DISCUSSION

In our previous work [12] about the preparation of methanol biodiesel catalyzed by new ionic liquid system had been informed. Reporting work devoted to the preparation of ethanol biodiesel from the sunflower oil by the transesterification reaction in the presence of the KOH and testing of different fuel blends with the glycerol ketal and pine oil additivities.

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

As known from the literature oxygenated compounds, such as glycerol ketals, pine oil (PO), 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. [14, 15].

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 I_2 per 100 g)	121.4±0.5			
Viscosity (cP)	34.1±0.5			
Flash point (°C)	265			
Pour point (°C)	+12			
Density (g/cm^3)	0.9186			

Considering the above indicated, the properties B10 blend (based on ethanol) in presence of cyclopentanone ketal and pine oil were studied. Pine oil can be regarded as one of the less viscous fuels in the likes of ethanol, methanol and consists of mainly cyclic terpene alcohols, known as terpineol ($C_{10}H_{18}O$) along with alpha-pinene ($C_{10}H_{16}$).
The physical properties of the diesel, sunflower biodiesel (B100), B10 blends with (or without) oxygenated additivities were investigated and the results are shown in Table 2, 3.

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

Properties	ASTM Methods	ASTM diesel	ASTM biodiesel	diesel	B10	B100
Relative density at 20°C, g/cm^3	D1298	0.8-0.84	0.86-0.9	0.837	0.85	0.88
Viscosity at 40°C, mm^2/s, min-max.	D445	2-5	3.5-5.0	3.44	3.4	4.6
Flash point, °C, min.	D93	65	>120	70	110	180
Cloud point (°C)	D2500	-12	<20	7	5	15
Pour point (^{0}C)	D2500	-15	<15	0	-10	3
Iodine value g (l_2)/100 g	-	60-135	<120	1.58	46.6	112.5
Sulfur, ppm, max.	D 975-14	15	15	50	35	0
Water and sediment, vol%, max.	D 975-14	0.05	0.05	0	0	0
Copper corrosion, 3 hr at 50°C, max.	D 975-14	№3	№3	№2	№1	№1
Cetane number, min.	D 975-14	40	47	53	52.3	48.3

Table 3 The physical properties of the **B10** with the **GK** and **PO**

Properties	B10	B10+PO (5%)	B10+GK (5%)	B10+GK (2.5%) and PO (2.5 %)
Relative density at 20°C, g/cm^3	0.88	0.85	0.86	0.86
Viscosity at 40°C, mm^2/s, min-max.	4.6	3.7	3.4	3.5
Flash point, °C, min.	110	110	105	105
Pour point (^{0}C)	15	-4	-4	-4
Cloud point (°C)	3	-14	-18	-19
Iodine value g (l_2)/100 g	112.5	47.3	45.5	47.7
Sulfur, ppm, max.	35	34	34	34
Water and sediment, vol%, max.	0	0	0	0
Copper corrosion, 3 hr at 50°C, max.	№1	№1	№1	№1

As seen from the tables 2, 3 density decreased for the B10+PO, B10+GK and B10+GK+PO blends. According to the dependence between the density and kinematic viscosity also significantly decreases in the presence of 5% oxygenated compounds in the blends. The significantly decreasing of the viscosity to positive influences on the flow and sprays characteristics in the engine.

The flash points are decreased for the biodiesel blends than pure biodiesel (B100). The cloud and pour points of the B10 are increased, but the presence of GK and PO are significantly decreased for the B10+PO, B10+GK and B10+GK+PO blends.
The amount of sulfur significantly was decreased as the percentage of biodiesel, cyclic ketal and pine oil in blends from the 50 up to 34 ppm, which is very important for the environment and human health. As shown in our experimental results, water and sediment, also copper corrosion parameters are excellent.
The density, viscosity, flash-, pour-, cloud points, copper corrosion and etc. properties of investigated fuel blends are according to the diesel fuel standard and suggested blends can be used in diesel engines without any problems.

4. CONCLUSION

The properties of diesel, B100, B10 blends with (or without) glycerol ketal and pine oil were investigated on the ASTM 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 fuel with (and without) oxygenated compounds.
An interesting aspect of the presented work is that this research was conducted for the first time on ethanol biodiesel.
Summarized the obtained data, we can note that the fuel blend B10 with (or without) oxygenated compounds have greater potentials for diesel engines than pure biodiesel (B100) and commercial diesel fuel.

REFERENCES

[1]]Barman, S.C., Kumar, R., Singh, G.S, et al. Assessment of urban air pollution and its health impact, *J. Enviro. Bio*., 31, 913-920, 2010.

[2] Janaun, J., Ellis, N. Perspectives on biodiesel as a sustainable fuel, *Renew.Sust. Energy Re*v.,14, 1312-1320, 2010.

[3] Meher, L.C., Vidya, D.S., Naik, S.N. Technical aspects of biodiesel production by transesterification-a review, *Renew. Sust. Energy Rev*., 10, 248-268, 2006.

[4] Miriam, D.T, Gonzalo, J., Jose, A.M., Elísabet, P., Mario, S. Glycerol ketals: Synthesis and profits in biodiesel blends, *Fuel*, 94, 614-6162, 2012.

[5] Edgar, L., Yiyan, L., Lopez, D.E., Suwannakaran, K., Bruce, D.A, James, G.J. Synthesis of biodiesel via acid catalysis, *Ind. Engineer. Chem. Res*., 44, 5353-5363, 2005.

[6] Nagarhalli, M.V., Nandedkar, V.M., Mohite, K.C. Emission and performance characterristics of Karanga biodiesel and its blends in a CI engine and its economics. *J. Engineer. Appl. Scien*., 5, 52-56, 2010.

[7] Nwafor, O.M.I. Emission characteristics of diesel engine operating on rapeseed methyl ester, *Renew. Enerergy*. 29, 119-129, 2004.

[8] Prasad, T.H., Reddy, K.H.C., Rao, M.M. Performance and exhaust emissions analysis of a diesel engine using methyl ester of oil with artificial neural network aid, *Inter. J. Engineer. Tech*., 2, 23-27, 2010.

[9] Kiakalaieh, A.T., Amin, N.A.S., Mazaheri, H. A review on novel processes of biodiesel production from waste cooking oil, *Appl. Energy*, 104, 683-710, 2013.

[10] Narasimharo, K., Lee, A., Wilson, K. Catalysts in production of biodiesel: A Review, *J. Bio. Mat. Bioenergy*, 1, 1-12, 2007.

[11] Lee, H.V., Juan, J.C., Taufiq-Yap, Y.H., Kong, P.C., Rahman, N.A. Advancement in heterogeneous base catalyzed technology: An efficient production of biodiesel fuels, *J. Renew. Sust. Energy*, 7, 1-47, 2015.

[12] Mamedov, I.G., Javadova, O.N., Azimova, N.V. Preparation of diesel fuel blends and study of their physical properties, *Proc. Univer. Appl. Chem. Biotech*., 2, 332-338, 2020.

[13] Singh, D., Sharma, D., Soni, S.L., Sharma, S., Sharma, P.K. A review on feedstocks, production processes, and yield for different generations of biodiesel, *Fuel*, 262, 1-15, 2020.

[14] Nanda, M.R., Zhang, Y., Yuan, Z., Qin, W., Ghaziaskar, H.S., Xu, C.C. Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review, *Renew.Sust. Energy Rev*.,56, 1022-1031, 2016.

[15] Prakash, T., Geo, V.E., Martin, L.J., Nagalingam, B. Evaluation of pine oil blending to improve the combustion of high viscous (castor oil) biofuel compared to castor oil biodiesel in a CI engine, *Heat Mass Tran*s., 55, 1491-1501, 2019.