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Testing of Some Ionic Liquids at the Synthesis of Biodiesel

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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 some ionic liquid catalysts. The yield was 98% using a 1:5 molar ratio of oil to alcohol at 55°C and in the quinoline-based ionic liquid catalyst. Important fuel exploitation properties of B20 and B50 fuel blends have been investigated. The obtained results showed that B20 and B50 blends have a greater advantage for diesel engines than B100 and fossil diesel fuels. The best results were demonstrated B20 fuel blend among the studied fuels.

Keywords: Transesterification, Biofuel, Biodiesel, Ionic Liquid, Catalyst

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1. INTRODUCTION

The promising and dynamic developing area of research in the field of biofuel production is the technology for producing biodiesel, which has a lot of significant advantages compared to petroleum products and other fossil fuels. The volume of biofuel production in the world is increasing on a large scale. If in 2021 the share of biofuels in the world production of fuel for road transport was 3.6%, then the International Energy Agency (IEA) predicts its increase to 15% by 2030 [1-8].

From the alternative type of fuels, biodiesel is a renewable resource consisting of fatty acid alkyl monoesters derived from vegetable oil, waste animal fats, waste cooking oil, etc. It is important to note that the combustion of biodiesel does not emit toxic substances that cause environmental problems due to the absence of aromatic, nitrogenous, and sulfurous compounds. 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 matter decreased by 13, 20 and 20 % respectively [9-15].

The production of biodiesel is mainly based on the FAME formation reaction. The transesterification reaction can be catalyzed by homogeneous alkali catalysts such as sodium hydroxide, sodium methoxide and potassium hydroxide or homogeneous acid catalysts such as sulfuric acid or hydrochloric acid, ionic liquids, etc. [16-17].

Considering the above, in the presented work, the transesterification reaction of sunflower oil with methyl alcohol in the presence of pyridine and quinoline based ionic liquid catalysts at first was carried out. The important exploitation properties of B20 and B50 fuel blends were estimated.

2. MATERIALS AND METHODS

All the chemicals for the synthesis of ionic liquids and biodiesel 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 B20 and B50 fuel blends were prepared by mixing diesel and biodiesel by volume (B20- 20% biodiesel and 80% diesel; B50- 50% biodiesel and 50% diesel).

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 $CDCl_3$ was used for the analysis of ethylene glycol ketal and fuel blends.

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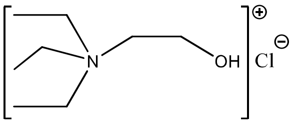
Fig. 1. The chemicals for the synthesis of ionic liquids

Fig. 2. The preparation of the ionic liquids

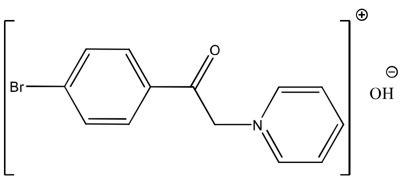
Preparation of 2-(triethyl-λ⁴-azanyl)ethan-1-ol chloride (TAEC).

An equimolar amount of the triethylamine and *2-chloroethanol* were dissolved in ethanol and the solution was kept under vigorous stirring at 70ºC for 24 hours. After cooling to room temperature, ethanol was evaporated from the mixture to give a basic TAEC ionic liquid catalyst.



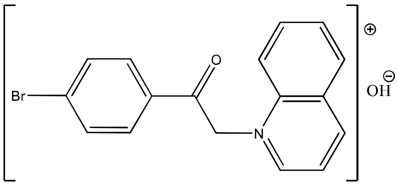
Preparation of 4-bromophenacyl pyridinium hydroxide (BPPH).

An equimolar amount of 4-bromophenacylpyridinium bromide and KOH was dissolved in ethanol and the solution was kept under vigorous stirring at 70ºC for 24 h. After cooling to room temperature, KBr was removed by filtration and ethanol was evaporated from the mixture to give a basic BPPH ionic liquid catalyst.



Preparation of 4-bromophenacyl quinolinium hydroxide (BPQH).

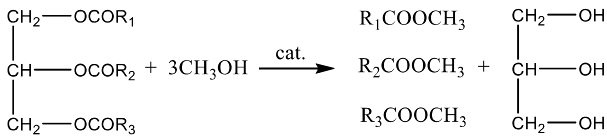
An equimolar amount of 4-bromophenacylquinolinium bromide and KOH was dissolved in ethanol and the solution was kept under vigorous stirring at 70ºC for 24 h. After cooling to room temperature, KBr was removed by filtration and ethanol was evaporated from the mixture to give a basic ionic liquid catalyst BPQH.



The procedure for the preparation of biodiesel

Sunflower biodiesel (B100) was synthesized by dissolving 0.5 g of BPPH (BPQH or TAEC) in 35 ml of methanol (CH_3OH) without heating at room temperature (Figure 3). After complete dissolution, 100 ml 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 55ºC. After stirring, the reaction mass was aged for at least 12 hours in a dividing funnel. The reaction mass was divided into two layers using a dividing funnel: the upper layer contained biodiesel and the lower layer glycerine. Untreated biodiesel was repeatedly washed with hot distilled water to remove catalysts. Water removal is achieved by distillation.

The yield of biodiesel was 83% and 98% when used the molar ratio of oil to methanol 1:5, as catalyst accordingly BPPH and BPQH.



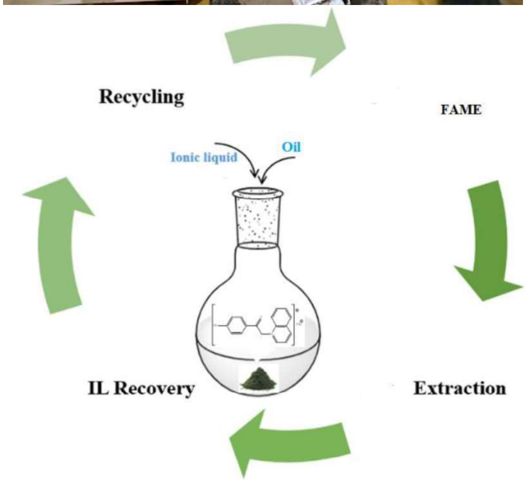


Fig. 3. The preparation of the biodiesel

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

3. RESULTS AND DİSCUSSİON

In our previous works [11-15], the preparation of methanol, and ethanol biodiesels catalyzed by a different catalytic system and testing of their exploitation properties had been informed.

In recent years, a new biomass processing technology using ionic liquid (IL) has been developed for the production of biofuels. Despite the high cost of ionic liquid catalysts, their main advantage is reuse and simple cleaning process [18-19].

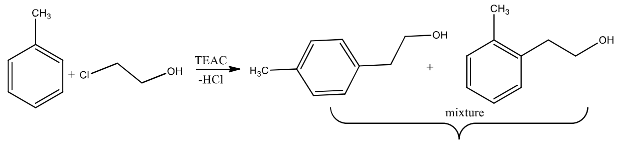
This work is devoted to the preparation of methanol biodiesel from the sunflower oil at presence of some ionic liquid systems and testing of their different exploitation properties.

The used sunflower oil 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 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			

At studying of biodiesel synthesis process in the presence of TEAC, it was determined that the catalyst is inactive in the transesterification reaction. However, as a result of our studies, it was demonstrated that TEAC catalyst is active in the alkylation reaction of toluene with 2-chloroethanol.



The yield of biodiesel was 83% at using the molar ratio of oil to methanol 1:5, as catalyst BPPH.

To increase the size of the cation in the ionic liquid, quinoline was used in the synthesis of the catalyst. The biodiesel yield was 98% using a 1:5 molar ratio of oil to methanol as the BPQH catalyst. Below is the given mechanism of the formation of biodiesel in the presence of an ionic liquid catalyst.

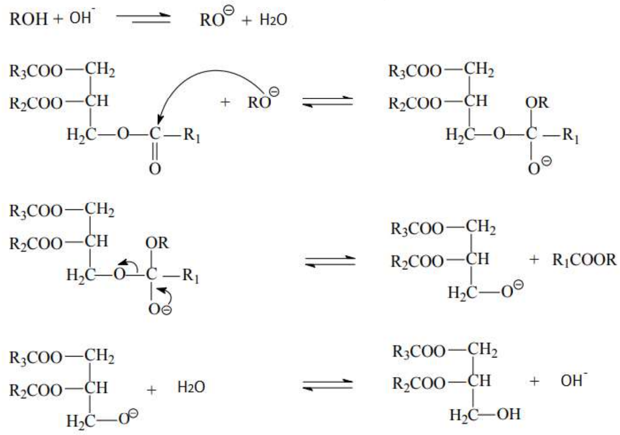


Fig. 4. Mechanisms of the transesterification in the presence of ionic liquid

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

Properties	ASTM Methods	ASTM diesel	ASTM biodiesel	diesel	B20	B50	B100
Relative density at 20°C, g/cm^3	D1298	0.8-0.84	0.86-0.9	0.837	0.859	0.864	0.88
Viscosity at 40°C, mm^2/s, min-max.	D445	2-5	3.5-5.0	3.44	3.60	3.78	4.1
Flash point, °C, min.	D93	65	>120	70	105	119	174
Cloud point (°C)	D2500	-12	<20	+7	+5	+10	+12
Pour point (^{0}C)	D2500	-15	<15	0	-5	+3	+6
Iodine value g (l_2)/100 g	-	60-135	<120	1.58	45.7	88.9	110.5
Sulfur, ppm, max.	D 975-14	15	15	50	33	27	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	43.4	44.1	45.6	48.5

As noted above, in recent years acidic and basic IL systems have been used for the synthesis of biodiesel. In most basic ILs, a substrate with a small free fatty acids (FFA) content is required to evade soap formation. The presented work catalytic activity of triethylamine (TEAC), pyridine (BPPH) and quinoline (BPQH) based ILs have been investigated.

In the continuation of the investigations, the properties of B20 and B50 fuel blends were studied. The exploitation properties of the diesel, sunflower biodiesel (B100), B20, and B50 blends were investigated and the results are shown in Table 2.

As seen in Table 2 density increased for B20 and B50 fuel blends. The density is a factor governing the quality of crude petroleum, but it is an uncertain indication of petroleum product quality unless correlated with other properties. According to the good afreement between the density and viscosity, kinematic viscosity also insignificantly increases as the percentage of biodiesel in the blends, but it is in the ASTM limit of 2-5 at 40°C.

The flash points are increased for the B20 and B50 blends than diesel fuel. It is also observed that flash points of pure biodiesels were higher than those of diesel and indicated blends. In this case, the biodiesel blends are hard to ignite with a higher flash point. But increasing flash point implies safer handling and storage.

The amount of sulfur significantly decreased as the percentage of biodiesel blends from 50 up to 27 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.

Considering the above indicated, we note that B20 and B50 fuel blends have high potential as an ecological pure fuel than simple diesel fuel.

The reported work was informed the new İLs catalytic systems, which have a positive influence on biodiesel production, and separation processes and it can be reused.

4. CONCLUSIONS

The presented work reported the application possibility of a new basic İLs catalytic system at the transesterification process. High yield (98%) was observed in the quinoline-based ionic liquid catalyst, but the triethylamine-based catalyst is active in the alkylation reaction of toluene with 2-chloroethanol.

The properties of diesel, sunflower biodiesel B20 and B50 blends were investigated on the ASTM standards. The best exploitation properties were demonstrated B20 fuel blend among the studied fuels.

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