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Testing of Glycerol Ketals as Components of B20and B50 Fuel Blends

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ABSTRACT

The reported work is devoted to testing glycerol ketals in fuel blends. Biodiesel was prepared from the sunflower oil by the FAME (fatty acid methyl ester) formation reaction in a new catalytic system medium. The re-esterification reaction was done in a 1:3 molar ratio of oil to alcohol at 55°C with a yield of 83%. The applying a new catalytic system positively influenced the foam production process at biodiesel washing. Due to the absence of the neutralization stage, the supported catalytic system can be reused after water removal through distillation.
Important fuel exploitation properties of diesel, biodiesel, and oxygenated diesel blends with the American Society for Testing and Materials (ASTM) standards had been investigated. The obtained results demonstrated that the fuel blends B20 and B50 with (or without) the glycerol ketals have great significance for diesel vehicles than B100 and diesel.

Introduction

Today we have different ecological disbalances, such as destroying the ozone protection zone, acidic rain problem, the emission of hazardous compounds into the environment, global warming, etc., and which formation of these problems have a significant role transport park of the world. Indicated ecological problems mainly are connected with emissions of carbon dioxide and toxic compounds from traditional fuels. The decreasing of natural oil, gas, etc. reserves is also a modern problem of the world [1-4].

The problems of exhaustion of fossil fuel resources, protection of the environment, and human health become the main drivers in searching for renewable and environmentally significant alternative energy sources. The problems of exhaustion of fossil fuel resources, protection of the environment, and human health become the main drivers in searching for renewable and environmentally important alternative energy sources. FAME (or biodiesel) is one of the competitive types of fuel for diesel vehicles. Biodiesel is the product of plant-vegetable oils, solid oils, and fat wastes after transesterification reactions.

Transesterification is a triglyceride reaction with small molecular mass alcohols in different reaction conditions to produce biodiesel and glycerol as the byproduct. The advantage of biodiesel or its blends for engines is low toxic gas emissions, high lubricity, easy biological decomposition, high cetane number, etc. İn the biodiesels contain are absent aromatic, nitrogen, and sulfur compounds, which are responsible for the formation of global ecological problems [5-9].

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During the last few years, biofuel production has grown significantly. The International Energy Agency (IEA) estimates the biofuel share in world road transport will be approximately 7% in 2030, while in 2004 it was only 1% [10, 11].

The improvement of the economic efficiency of the biodiesel formation process is a significant application of the byproduct glycerol. In literature demonstrated the uniqueness of glycerol for the synthesis of surfactants, cosmetics, plastics, use as solvents in organic synthesis, etc. One of the interesting applications of glycerol is the obtaining of glycerol ketals as additives to fuels [12-32].

The fuel properties are strongly dependent on the purity of biodiesel. İn the biodiesel production industry frequently are applied alkali or acid catalysts. Using the traditional alkaline/acid reaction conditions has a disadvantage in the separation, the regeneration of the catalyst, also taken place pollution environment, and equipment corrosion [33, 34].

Considering the above indicated, un this work reported the production of biodiesel from sunflower oil in the presence of a new catalytic system, preparing the B20, B50 fuel blends with/without the glycerol ketals and investigating their exploitation properties.

Experimental Section

Materials

The investigated diesel sample and sunflower oil were purchased from fuel stations/or markets in Baku, Azerbaijan. The B20 and B50 fuel blends were prepared on the weight ratio of diesel and biodiesel, and their exploitation properties were characterized in accordance with the American Standard for Testing and Material (ASTM) methods (Table 2).

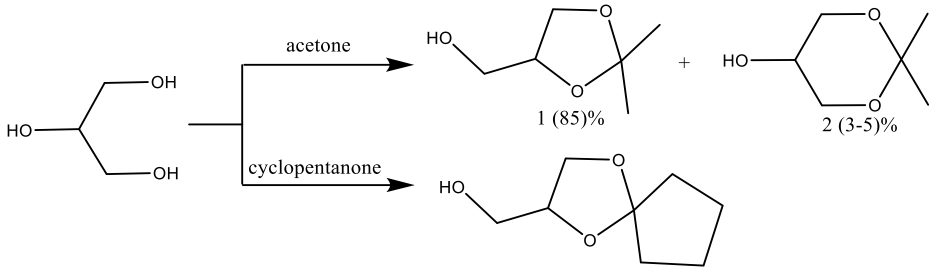
Experiment

Sunflower FAME (B100) was synthesized by dissolving 0.5 g of KOH + 0.5 g 4-bromophenol pyridinium hydroxide (BPPH) in 75 ml CH_3OH without heating. After adding 100 g of oil the transesterification process was done for 3 hours under reflux at 55ºC (rpm ~ 1000) in a three-neck flask supplied with a reflux condenser and magnetic stirrer. In a funnel was formed two layers, the upper layer is biodiesel and the lower layer is glycerol, both layers were collected separately. Purification of crude biodiesel was carried out with hot distilled water and this was repeated several times. The yield was 83% in the case molar ratio of oil to alcohol 1:3 at 55°C.

Pure glycerol (25 g), acetone (100) ml and p-toluenesulfonic acid (0.75 g) were added in a 500 ml three-neck glass flask supplied with a condenser and magnetic stirrer. The mixture was stirred under 30°C for 120 hours. After finishing, the reaction mass was neutralized with sodium acetate (0.5 g). After filtration of the solid part and evaporation of the acetone, the ketal **1** was obtained by vacuum distillation (yield 85%).

A similar experiment for the cyclopentanone in benzene at 60°C had been carried out, and the yield of ketal 3 was 96% (Fig. 1).

4-Bromophenacyl pyridinium hydroxide (BPPH) 4 was prepared by refluxing 10 mmol 4-phenacyl bromide and 10 mmol pyridine in 50 ml toluene. After the formation of quaternary pyridinium bromide salt added 10 mmol KOH for the synthesis of BPPH (Fig. 2).



3 (96)%

Fig. 1. The synthesis scheme of ketal **1** and **3**

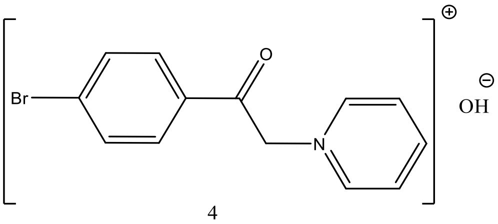


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Fig. 2. 4-Bromophenacyl pyridinium hydroxide (BPPH)

Analysis

NMR experiments for all samples 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). NMR-grade acetone-d_6, and $CDCl_3$ were used for the solutions of diesel, biodiesel, ketals, and catalyst.

The cetane numbers for fuel blends were calculated according to the literature [35-37].

Results and Discussions

The properties of biodiesel are dependent on the oils-fats compositions and these compositions have a significant role in the exploitation parameters of biodiesel, such as cetane number, viscosity, cloud temperature, etc. The physicochemical properties of the sunflower oil are shown in Table 1.

Table 1. Physicochemical properties of the refined sunflower oil

Fatty acid composition (wt.%)	16:0	18:0	18:1	18:2
	7.4	5.0	29.3	58.3
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		
Flashpoint (°C)		265		
Pour point (°C)		+12		
Density (g/cm^3)		0.9186		

The exploitation properties of the diesel, sunflower biodiesel (B100), also B20, and B50 blends were studied and the obtained data are shown in Tables 2 and 3.

Table 2. The exploitation properties of biodiesel from sunflower oil, its blends and diesel

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	0.886
Viscosity at 40°C, mm^2/s, min-max.	D445	2-5	3.5-5.0	3.44	3.49	3.87	4.15
Flashpoint, °C, min.	D93	65	>120	70	75	87	137
Cloud point (°C)	D2500	-12	<20	7	9	10	11
Pour point (^{0}C)	D2500	-15	<15	0	2	5	1
Iodine value g (I_2)/100 g	-	60-135	<120	1.58	47.69	88.97	113.86
Sulfur, ppm, max.	D 975-14	15	15	50	38	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	45.1	45.6	48.5

Table 3. The exploitation properties of the biodiesel blend with the ketals **1** and **3**

Properties	B20+1 (20%)	B20+3 (20%)	B20+1 (10%) and 3 (10%)	B50+1 (20%)	B50+3 (20%)	B50+1 (10%) and 3 (10%)
Relative density at 20°C, g/cm^3	0.857	0.881	0.887	0.869	0.893	0.889
Viscosity at 40°C, mm^2/s, min-max.	3.55	3.77	3.84	4.06	4.44	4.48
Flashpoint, °C, min.	72	83	78	90	101	97
Cloud point (°C)	6	8	2	8	9	6
Pour point (^{0}C)	-1	1	-5	3	4	1
Iodine value g (I_2)/100 g	46.71	46.21	45.30	87.33	86.83	85.87
Sulfur, ppm, max.	35	33	30	24	21	20
Water and sediment, vol%, max.	0	0	0	0	0	0
Copper corrosion, 3 hr at 50°C, max.	№1	№1	№1	№1	№1	№1

On the based obtained results (Tables 2 and 3) we can note that density increased for the B20 and B50 blends. The kinematic viscosity also increases as the percentage of FAME in the fuel blends, but it is in the ASTM limit of 2-5 at 40°C.

The significant increase in viscosity is undesirable for diesel fuels as a result of the negative influences on the flow and spray characteristics. The kinematic viscosities of B20 and B50 are within the scale limit of the diesel fuel standard and suggested blends can be usable in internal combustion engines (ICE) without any problems.

The flash points are increased for the B20 and B50 blends than diesel fuel. As seen from the obtained data flash point for pure biodiesel is higher than for diesel and indicated fuel blends. That means in this case the biodiesel blends are hard to ignite with a higher flash point. But increasing flash points have significance for safer transportation and storage.

For the various blends cloud and pour points are insignificantly increased in the presence of volume percentages of biodiesel in the diesel (B20, B50), but obtained results are normal for the diesel blends.

Especially we want to note that, interesting results were observed for the B20 and B50 blends with glycerol ketals. In all cases, cloud and pour points are decreased. For the B20+1 (10%) and 3 (10%), the blend pour point decreased up to -5°C.

In the content of the investigated diesel, there are no unsaturated compounds. It was confirmed by the experimental iodine value determination and ^{1}H NMR methods, but unsaturation in the biodiesel blends (B20, B50) was within the ASTM-specified range (Fig. 3).

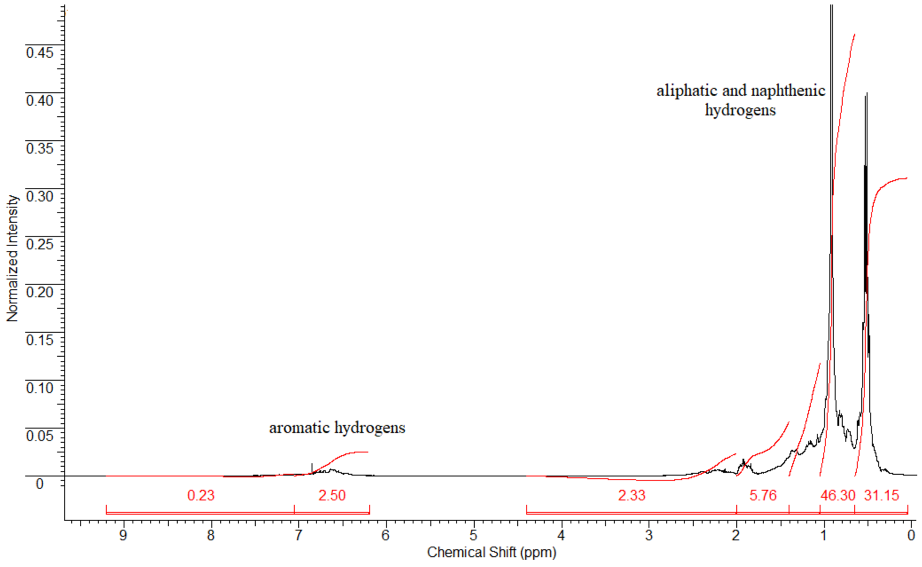

Fig. 3. ^{1}H NMR spectra for the diesel fuel

The significantly decreased value of sulfur as the percentage of FAME in diesel (B20, B50) from 50 up to 27 ppm, from 35 up to 20 ppm for the B20, B50 blends with glycerol ketals, which is very demonstrable for the environment and human health.

Excellent values were obtained for water, sediment, also copper corrosion parameters. The absence of water also is a good view from the ^{1}H NMR spectrum of biodiesel and ketals (Figs. 4 to 6).

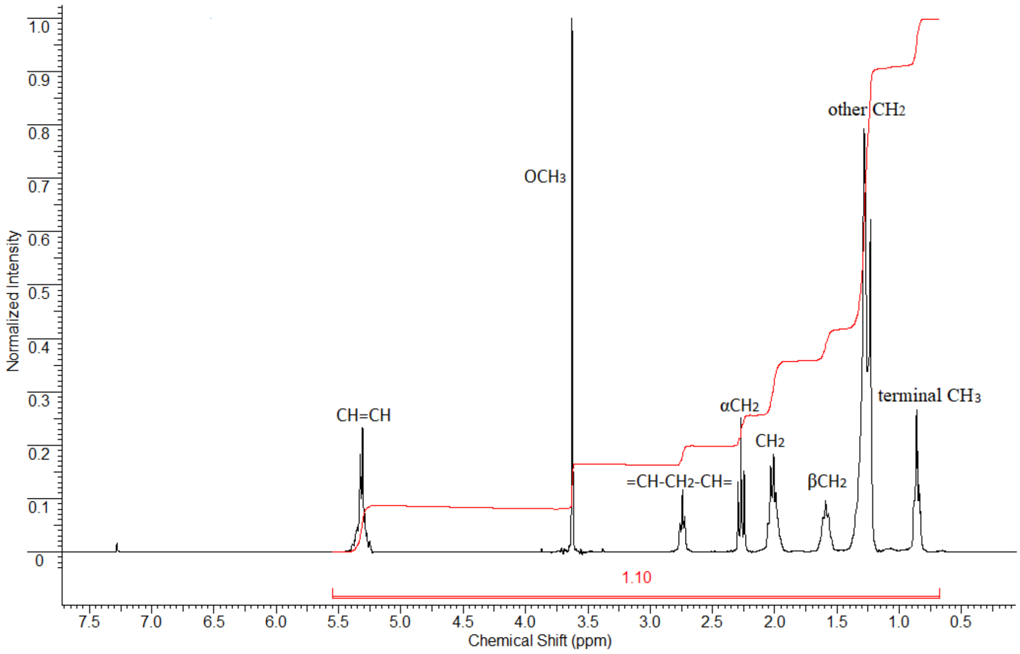

Fig. 4. ^{1}H NMR spectra for the biodiesel

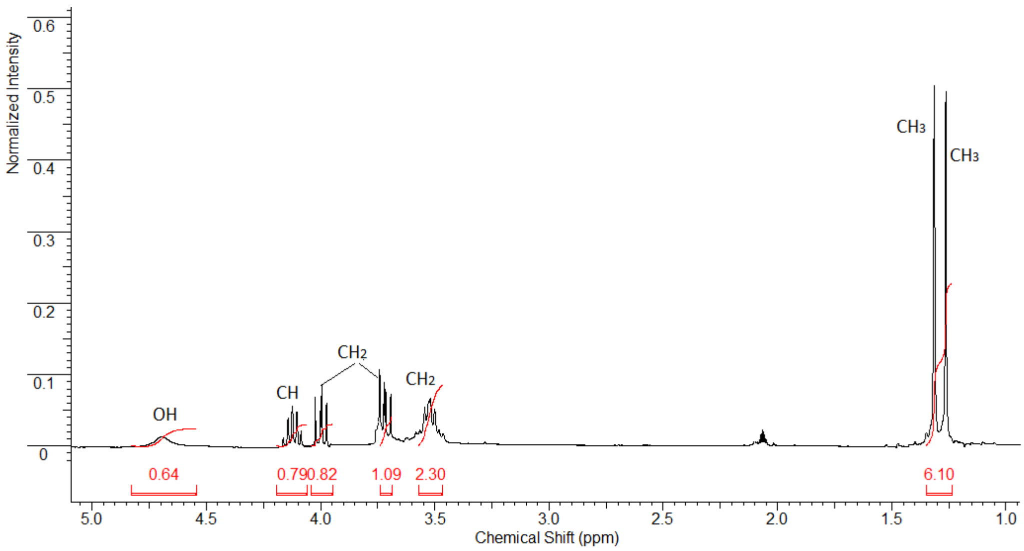

Fig. 5. ^{1}H NMR spectra for the ketal 1

Besides it, the presence of a free hydroxyl group in the ketals serves to improve oxidation stability and keep blend content under quality parameters.

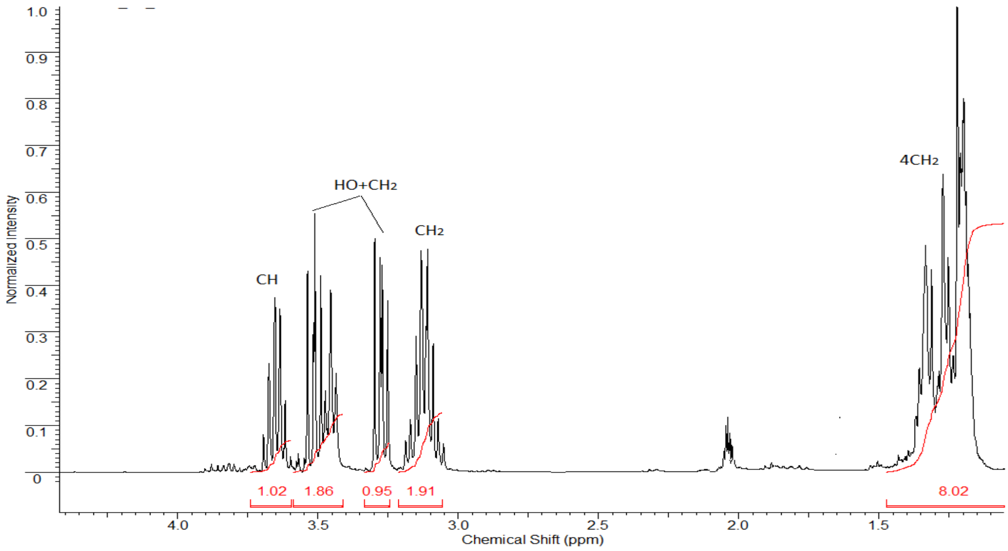

Fig. 6. ^{1}H NMR spectra for the ketal 3

The cetane numbers of B20 and B50 blends insignificantly were decreased, but higher than 45. It does not significantly influence to exploitation properties of investigated samples.

It the important to note that, the octane number of ketals is much higher than commercial gasoline. For example, solketal (1) has octane number 98, therefore it is an excellent octane number improver for gasoline.

A significant advantage of the proposed catalytic system is the absence of foam formation during the cleaning process of biodiesel. In addition, the proposed method omits the stage of catalyst neutralization; therefore, the catalytic system can be reused upon water removal. The biodiesel yield comprises 61 % and 38 % upon the second and third use of the catalyst, respectively.

Conclusions

The presented work has reported the applications of cyclic glycerol ketals in diesel-biodiesel blends. FAME was prepared from the sunflower oil by the re-esterification reaction in a new ionic liquid catalytic system medium with a yield of 83%. The application of the proposed catalytic system reduces the amount of foam formation by biodiesel washing and it can be recycled. Important exploitation properties of fuel blends with (or without) the glycerol ketals compounds were tested. According to the experimental results, we can note that the fuel blends B20 and B50 have high importance for diesel engines than, B100 and diesel.

Declaration of interest

The authors declare no conflict of interest regarding the publication of this article. The final manuscript has been read and approved by all the co-authors.

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