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Pine oil and glycerol ketal as components of B10 fuel blends

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The main exploitation fuel properties of the B10 blends in the presence (or absence) of glycerol ketal and pine oil additivities have been examined and studied by the ASTM standards. Methanol (or ethanol) biodiesel has been obtained by the transesterification reaction of sunflower oil in the presence of potassium hydroxide. The conversion is 91 and 96% using 1:3 molar ratio of oil to alcohols at 65 and 75°C respectively. The results obtained are demonstrated that the investigated B10 fuel blends with oxygenated compounds have greater potential for diesel engines than, B100 and fossil diesel. The oxidation properties of B10 fuel blends are estimated using NMR spectroscopy. İn the presented workit can be concluded that glycerol ketal and pine oil can be successfully used in diesel fuels as antioxidant additivity.

Keywords: Biofuel, B10 blends, Glycerol, Pine oil, Transesterification

Despite the high toxic emissions of diesel fuels, nowadays they are used in city buses, heavy goods transport, locomotives, electric generators, etc. Therefore, one of the challenges is to improve the environmental performance of diesel fuels. For the solving of these problems, one of the ways is using biodiesel in diesel fuels, which is technically feasible, environmentally acceptable, and readily available. In the last years, the biodiesel industry has gained considerable attention due to environmental issues resulting in its production increases. Considering these requirements, vegetable oils or animal fats are the main sources of biodiesel production. Indicated sources are widely available and they are renewable. Potential advantages of alternative biodiesel for internal combustion engines (ICE) are low emissions, longer engine life due to better lubrication, biological decomposition, high cetane number, absence of toxic aromatic, nitrogen and sulfur compounds, etc. Moreover, green plants are sequestering more carbon dioxide from the atmosphere, than emissions at biodiesel burning. They help to decrease carbon dioxide in the atmosphere. The main disadvantage of biodiesel is its price, which is higher than petroleum diesel[1-8].

Besides, the main problem in the biodiesel industry is the utilization of glycerol are produced as a byproduct. However, the purification cost of crude glycerol for conventional applications doesn't economical. Consequently, it is essential to develop valuable compounds to make the overall biodiesel process costs competitive. Glycerol chemistry has significant the interest of the scientific society and several reviews have appeared in the literature. Given these, we can note that glycerol acetals and ketals have received considerably the most attention, which can find applications as fuel additives[9-11].

In addition, we can note that the alcohols also can be used as fuel additives in the ICE, which is regarded as the simplest and attractive method, though complete replacement of fuels is impossible. In the published works were informed that using less viscous fuel, in the likes of alcohols, such as essential oils has also garnered much attention in recent times. As alcohols, these compounds have low viscosity and unlike alcohols, they have caloric value with diesel[12,13].

Considering the above, in the presented work, the transesterification reaction of sunflower oil with methanol and ethanol in the presence of KOH was carried out. The important operational properties of B10 fuel blends on the basis of FAME and FAEE were tested in the presence (or absence) of glycerol ketal and pine oil. The oxidation properties of B10 fuel blends are estimated by using NMR data.

Experimental Section

Materials and instrumentation

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 oilwere 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 (Fig. 1).

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 (Top Spin 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.

Fig. 1 — Pine oil and glycerol ketal.

Fig. 2 — Preparation of the biodiesel.

The purity of the synthesized compounds was confirmed by thin-layer chromatography (TLC) on commercial aluminum-backed plates of silica gel (60 F254), iodine vapour was used as a visualizing agent, eluent- 5:2 hexane/ethyl acetate.

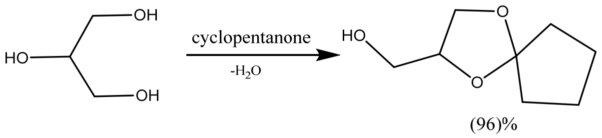
Procedure for preparation of biodiesel

Transesterification of sunflower oil with methanol (or ethanol) (B100) was carried out by using of standard literature method[14]. The conversion of biodiesel was 91 and 96% accordingly when using the molar ratio of oil to ethanol 1:3 (Fig. 2).

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

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%.



The oxidation stability of diesel and B10 blends was tested by ASTM D 2274-03a (Fig. 3).

Results and Discussion

In our previous works[14,15] about the preparation of methanol and ethanol biodiesel catalyzed by a new ionic liquid system (or KOH) had been informed.This work is devoted to the preparation of methanol and ethanol biodiesel from the sunflower oil, testing their different exploitation properties with (or without) the glycerol ketal and pine oil additivities.

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

On the based literature information, we can note that 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.[9-11]. Considering the above indicated, the properties of B10 blends (based on methanol and ethanol) in the presence (or absence) of glycerol 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 alpha-terpineol ($C_{10}H_{18}O$) along with alpha-pinene ($C_{10}H_{16}$)[16].

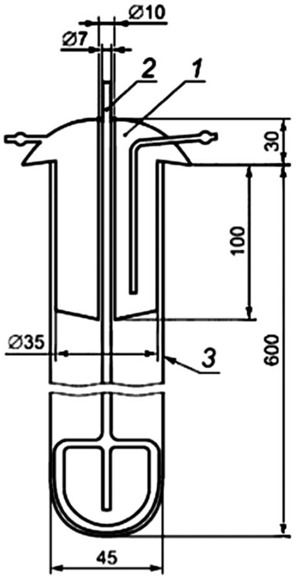
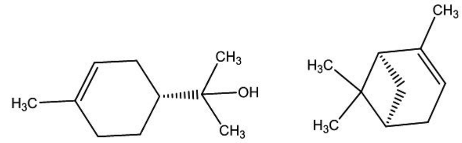


Fig. 3 — Oxidation cell.



The exploitation properties of the diesel, sunflower biodiesel (B100), B10 blends with (or without) glycerol ketal-pine oil additivities were investigated and the results are shown in Table 2, 3.

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			

Table 2 — Exploitation properties of B100, B10 and diesel fuels.

Properties	ASTM Methods	ASTM		diesel	B10		B100	
		Diesel	Biodiesel		FAME	FAEE	FAME	FAEE
Relative density at 20°C, g/cm^3	D1298	0.8-0.86	0.86-0.9	0.84	0.85	0.85	0.88	0.89
Viscosity at 40°C, mm^2/s, min-max.	D445	2-5	3.5-5.0	3.44	3.3	3.4	4.1	4.6
Flash point, °C, min.	D93	65	>120	70	113	110	180	179
Cloud point (°C)	D2500	-12	<20	+7	+2	+5	+15	+17
Pour point (°C)	D2500	-15	<15	0	-15	-10	0	+3
Iodine value g (l_2)/100 g	-	60-135	<120	1.58	46.1	46.6	112.5	111.8
Sulfur, ppm, max.	D 975-14	15	15	50	35	33	0	0
Water and sediment, vol%, max.	D 975-14	0.05	0.05	0	0	0	0	0
Copper corrosion, 3 hr at 50°C, max.	D 975-14	№3	№3	№2	№1	№1	№1	№1
Cetane number, min.	D 975-14	40	47	43	43.3	43.3	43.5	45.5

Table 3 — Exploitation properties of the B10 with the GK and PO.

Properties	B10		B10		B10	
	FAME + PO (5%)	FAEE + PO (5%)	FAME + GK (5%)	FAEE + GK (5%)	FAME +PO (2.5%) and GK (2.5 %)	FAEE +PO (2.5%) and GK (2.5 %)
Relative density at 20°C, g/cm^3	0.85	0.85	0.86	0.86	0.86	0.86
Viscosity at 40°C, mm^2/s, min-max.	3.7	3.7	3.3	3.4	3.4	3.5
Flash point, °C, min.	114	110	100	105	105	106
Cloud point (°C)	-4	-4	-3	-4	-5	-4
Pour point (°C)	-17	-14	-16	-18	-14	-19
Iodine value g (l_2)/100 g	47.3	46.8	45.5	45.1	46.3	46.1
Sulfur, ppm, max.	34	32	34	32	34	34
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
Cetane number, min.	44.6	44.6	42.8	43.0	43.0	43.6

As seen from Tables 2 and 3 density increased for all B10 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. The kinematic viscosity of biodiesel is also higher than that of diesel. Therefore, the kinematic viscosity of B10+PO, B10+PO+GK increases with an increase in the proportion of biodiesel, although remaining within 2–5 mm^2/s at 40°C and meeting ASTM requirements. However, the viscosity of all B10 blends almost equals that of diesel, which indicates their suitability for diesel engines.

The flashpoints are decreased for the biodiesel blends than pure biodiesel (B100).The cloud and pour points of all B10 blends at the presence of GK and PO are significantly decreased (up to -19°C).

The amount of sulfur significantly was decreased as the percentage of biodiesel blends from 50 up to 32 ppm, which is very important for the environment and human health. As seen obtained experimental results, water sediment, also copper corrosion parameters were excellent.

The density, viscosity, flash-, pour-, cloud points, copper corrosion, 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.

The cetane number, one of the key indicators for diesel fuels, has risen in all cases, except at the presence of high-octane number oxygenated components (FAME+GK, FAEE+GK, FAME+PO+GK).

The oxidation stability of biodiesels was tested by ASTM D 2274-03a and estimated by using NMR data[17].

Amount of $A_{C18:2}$ and$A_{C18:3}$ (di- and triunsaturated FAME or FAEE) calculated by

$$A_{C18:2} = 0.5\,(I_{exper,bisallylic} - 4\,A_{C18:3})$$

in which $I_{exper,bisallylic}$ is the experimentally determined integration value for the bis-allylic protons at 2.7–2.8 ppm.

$$A_{C18:3} = I_{exper,methyl,C18:3}/(I_{exper,methyl,C18:3}+I_{exper,methyl,rest})$$

in which $I_{exper,methyl,C18:3}$ is the integration value of the terminal CH_3 protons of linolenic acid and $I_{exper,methyl,rest}$ is the integration value of the terminal CH_3 protons of all other fatty acids in the sample at 0.8-0.9 ppm.

The amount of di- and triunsaturated FAME (or FAEE) before and after oxidation are given in Table 4.

The oxidation stability of diesel and B10 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 5).

As seen from Table 5, oxidation stability of diesel is more than B10 fuel blends but less than B10 FAME+GK and FAEE+GK during the oxidations at 16 hours, at 95°C. This is due to the fact that ketal protects the fuel from oxidation and increases the integrated intensity of the aromatic, olefin, naphthenic and paraffinic parts by destroying and oxidizing itself.

Based on the NMR spectra before and after oxidation, we can note that the first occur destruction of glycerol ketal with the formation of glycerol and alkyl cyclopentanes. Then acrylic acid is formed as a result of glycerin conversion reactions. Cycloparaffin, olefin and acid fragments formations in a mixture have influenced the increase of integral intensities in aromatic, olefin, and paraffinic regions of NMR spectra. This is confirmed by the absences of the ketal fragment in the ^1H NMR spectrum at 3.6-4.3 ppm.and the formation of new olefin and acid carbonyl signals in the ^{13}C NMR spectrum at 127-175 ppm after oxidation (Fig. 4-7). The following is given a plausible scheme of the destruction and oxidation reactions of ketal.

Table 4 — Amount of di- and triunsaturated FAME (or FAEE) before and after oxidation

	FAME		FAEE	
	$A_{C18:2}$	$A_{C18:3}$	$A_{C18:2}$	$A_{C18:3}$
Before	64	1	62	1
After	13	0	24	0

Table 5 —Oxidation stability of diesel and B10 blends

	Diesel	B10		B10		B10		B10	
		FAME	FAEE	FAME + PO (5%)	FAEE + PO (5%)	FAME + GK (5%)	FAEE + GK (5%)	FAME +PO (2.5%) and GK (2.5 %)	FAEE +PO (2.5%) and GK (2.5 %)
Before (OS_{NMR})	44.8	32.1	114.1	31.4	32.9	37.5	37.8	37.2	45.5
After (OS_{NMR})	48.9	107.7	130.5	63.9	97.1	32.6	16.7	77.1	65.6
Oxidation indicator	9	235.9	14.4	103.5	202.5	-13	-55.8	107.3	44.2

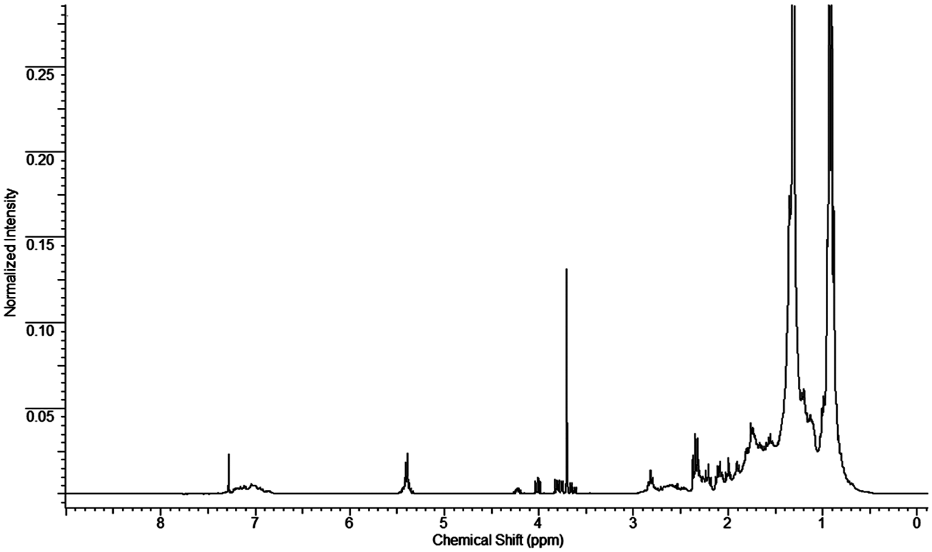


Fig. 4. — ^{1}H NMR spectrum of FAME+GK before oxidation.

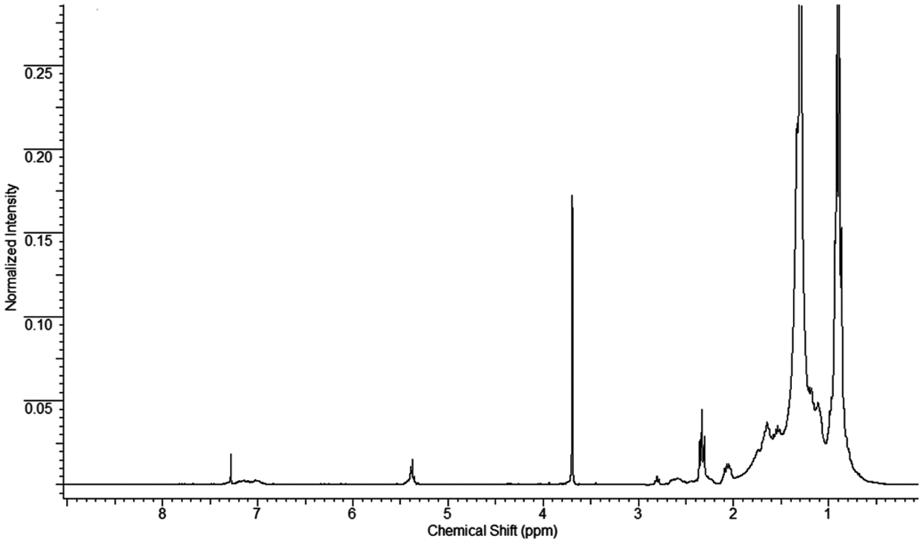


Fig. 5. — ^{1}H NMR spectrum of FAME+GK after oxidation.

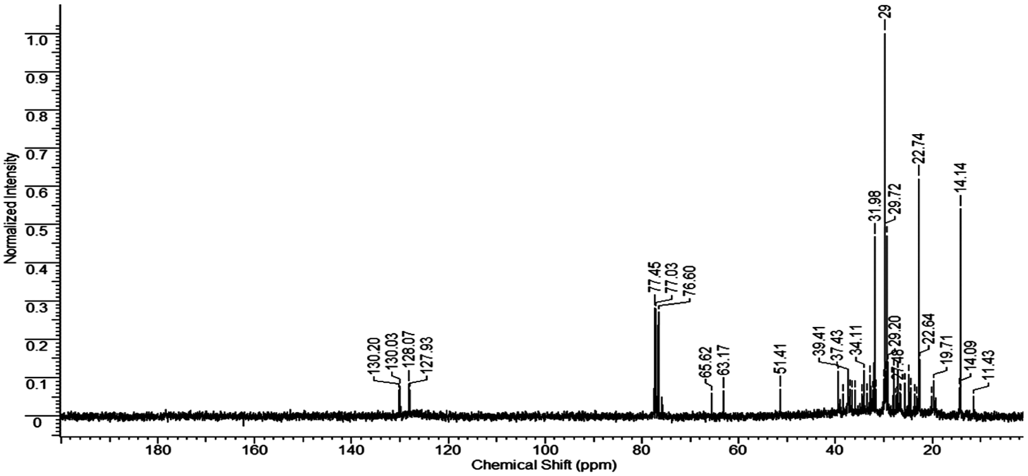


Fig. 6. — ^{13}C NMR spectrum of FAME+GK before oxidation.

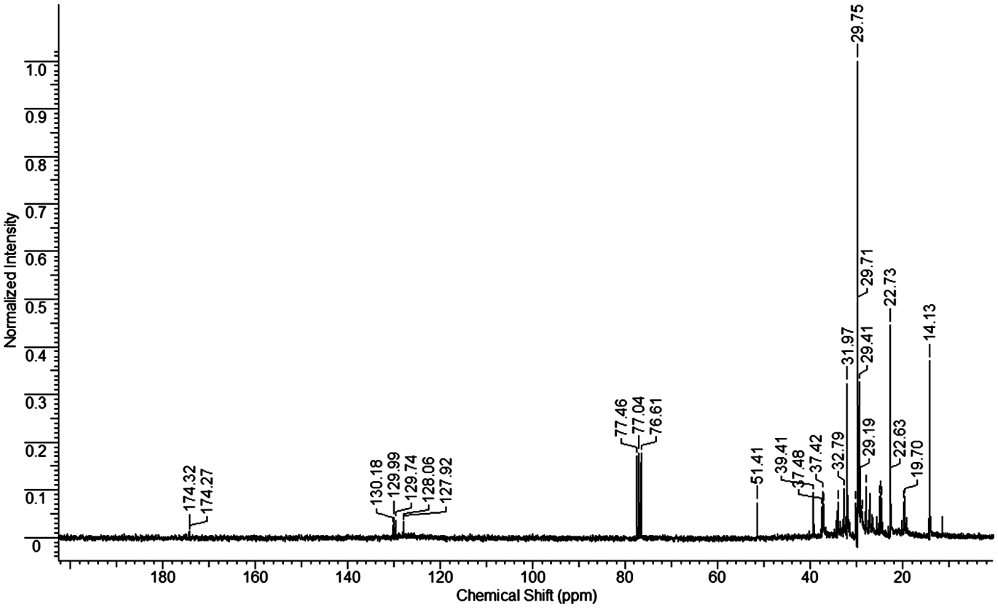


Fig. 7 — ^{13}C NMR spectrum of FAME+GK after oxidation.

It is also important to note that the oxidation stability of FAME+PO, FAME+PO+GK and FAEE+PO+GK is more than that of FAME.

As a result of our detailed studying, it can be concluded that glycerol ketal and pine oilcan be successfully used in diesel fuels as antioxidant additivity.

Conclusion

The exploitation properties of diesel, B100, B10 blends with (or without) glycerol ketal and pine oil are investigated on the ASTM standards.

Obtained results have demonstrated the exploitation accessibility of important fuel's properties- such as density, viscosity, amount of sulfur, copper corrosion, flash-, pour- and cloud points for B10 fuel with (and without) oxygenated compounds. Our studying again confirms the importance of NMR spectroscopy in the estimation of the oxidation stability of fuel blends.

Summarizing the obtained results, we can note that the fuel blend B10 with (or without) oxygenated compounds has greater potential for diesel engines than pure biodiesel (B100) and commercial diesel fuel.

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