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Testing of *n*-butanol and eucalyptus essential oil as additivities of cottonseed biodiesel-diesel blends

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The B10 fuel blend in the presence (or absence) of n-butyl alcohol and eucalyptus essential oil additivities by the ASTM standards has been tested. As seen our results, these oxygenated compounds can be successfully used in B10 fuel blends as additives to improve exploitation properties. Methanol-based biodiesel has been synthesized by the transesterification reaction of technical cottonseed oil in the presence of potassium hydroxide, with a maximum yield of 64% at a molar ratio of oil to alcohol of 1:3, at 65°C. The oxidizing stability of the B10 fuel blends with (or without) additivities has been evaluated using the NMR spectroscopy method. Our experimental results demonstrated that investigated B10 fuel blend with oxygenated compounds has a high potential for diesel engines than B100 and petroleum diesel. The best results demonstrate the B10+n-Butanol fuel blend.

Keywords: Biofuel, Eucalyptus essential oil, *n*-Butanol, Transesterification

To solve the energy problems of the world, are used a large number of non-renewable energy resources (natural gas, petroleum, coal, etc.) with toxic emissions in different areas of transportation systems and industries. The increasing consumption of petroleum products negatively influences the environment by releasing hazardous chemicals at combustions, mainly CO, CO_2, SO_2, NOx, smoke, and other types of cancerogenic compounds. Indicated emissions cause greenhouse gas effects resulting in global warming, climate change, and other ecological catastrophes at an alarming rate. To overcome the aforesaid problems, it has become inevitable to search the sustainable resources. Using effectible renewable energy types with minimum environmental impact is an important requirement in the energy sector. For the diesel engine biodiesel is considered a significant alternative biofuel, due to its environmental benefits and simple production from renewable resources[1-10].

In addition, we can note that alcohols and essential oils can be used as fuel additives in internal combustion engines (ICE), which is regarded as the simplest and most attractive method, though complete replacement of fuels is impossible. As cited in experimental works, the alcohols and essential oils contain a large amount of oxygen which is responsible for complete fuel combustion and improve the performance of diesel engines[11-13].

Considering the above, in the presented work the transesterification reaction of technical cottonseed oil with methanol in the presence of KOH was carried out. Important exploitation properties of the B10 fuel blends were tested in the presence (or absence) of *n*-butanol and eucalyptus essential oil. The antioxidant properties of oxygenate compounds were studied using NMR data.

Experimental Section

Materials and instrumentation

Methanol, *n*-butanol and KOH were obtained from commercial sources (Aldrich) and used as received. The tested diesel fuel, also technical cottonseed oil (Fig. 1) was purchased at a fuel station and cottonseed oil refinery plant in Azerbaijan. The B10 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 ^{1}H NMR 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 NMR chemical shifts were referenced to internal

Fig. 1 — Technical cottonseed oil.

Fig. 2. — Preparation of the biodiesel.

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 fuel blends.

Procedure for preparation of biodiesel

Transesterification of technical cottonseed oil with methanol was carried out by using of standard literature method[14]. The yield of biodiesels was 64% using a molar ratio of oil to methanol of 1:3 (Fig. 2).

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

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

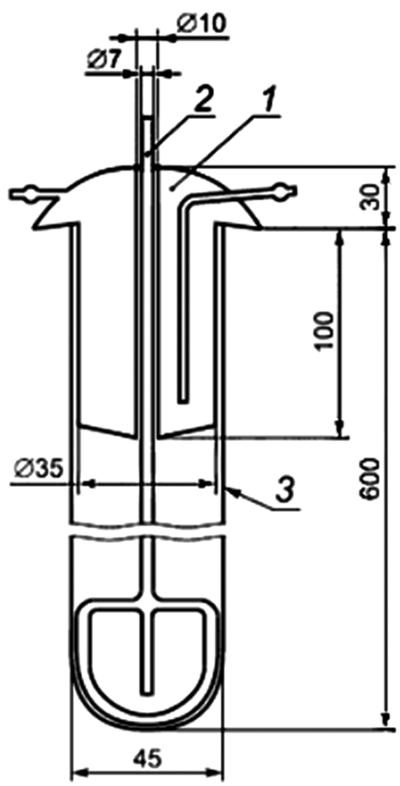


Fig. 3 — Oxidation cell.

Results and Discussion

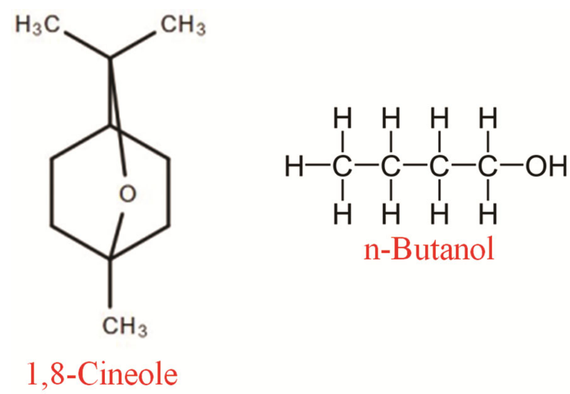
Our previous works[14-16] reported the synthesis of methanol and ethanol biodiesels catalyzed by a novel ionic liquid (or KOH) system and tested their exploitation properties. This work is devoted to the preparations of methanol biodiesel from the technical cottonseed oil, testing its fuel blend properties with (or without) the *n*-butanol and eucalyptus essential oil additivities. The used feedstock technical cottonseed oil physicochemical properties are shown in Table 1.

On the based literature information, we can note that oxygenated compounds, such as *n*-butanol, eucalyptus essential oil, 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.[14,16,17,18]. Considering the above indicated, the properties of the B10 blends in the presence (or absence) of *n*-butanol and eucalyptus essential oil were studied. Eucalyptus oil mainly contains 1,8-cineole (90%) and contains around 10.4% oxygen by weight (in the content of the n-butanol amount of oxygen is 21.6%) (Structure 1). The boiling point and flash point of 1,8-cineole (or *n*-butanol) are 176°C (117.4ºC) and 49°C (34°C) respectively[19]. These data indicate that the flash point of the prepared B10 fuels should be sufficiently low.

The exploitation properties of the diesel, technical cottonseed oil biodiesel (B100), B10 blends with (or without) oxygenate additivities were investigated and the results are shown in Tables 2 and 3.

As seen from Tables 2 and 3 density is not significantly 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 (B100) is also higher than that of diesel. But, the kinematic viscosity of B10+Bu, B10+EO and B10+Bu+EO significantly decreases (for B100- 4.1, for diesel- 3.4, for B10+Bu+EO- 3.2, for B10+EO- 3.1 and for B10+Bu- 2.9 mm^2/s). It is very important for the transportation of fuel from the tank to engine.

The flashpoints are decreased for the biodiesel blends than for pure biodiesel (B100). Especially we



Structure 1

Table 1 — Major fatty acids and physical properties of the technical cottonseed oil

Fatty acid composition (wt.%)	16:0	18:0	18:1	18:2
	24.4	2.2	17.2	55.5
Acid value (mg of KOH/g)		0.5±0.5		
Saponification value (mg KOH/g)		191.8±0.5		
Iodine value (g I_2 per 100 g)		106.5±0.5		
Viscosity (cP)		50.9±0.5		
Flash point (°C)		293		
Pour point (°C)		0 ÷ -2		
Density (g/cm^3)		0.9275		

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

Properties	ASTM Methods	ASTM diesel	ASTM biodiesel	diesel	B10 FAME	B100 FAME
Relative density at 20°C, g/cm^3	D1298	0.8-0.86	0.86-0.9	0.84	0.85	0.88
Viscosity at 40°C, mm^2/s, min-max.	D445	2-5	3.5-5.0	3.44	3.3	4.1
Flash point, °C, min.	D93	65	>120	70	120	174
Cloud point (°C)	D2500	-12	<20	+7	+2	+12
Pour point (^{0}C)	D2500	-15	<15	0	-10	+6
Iodine value g (l_2)/100 g	-	60-135	<120	1.58	45.3	110.5
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	43	43.0	43.5

Table 3 — Exploitation properties of the B10 with the Bu and EO

Properties	B10 FAME + Bu (5%)	B10 FAME + EO (5%)	B10 FAME + Bu (2.5%) and EO (2.5 %)
Relative density at 20°C, g/cm^3	0.85	0.86	0.86
Viscosity at 40°C, mm^2/s, min-max.	2.9	3.1	3.2
Flash point, °C, min.	86	105	106
Cloud point (°C)	0	+6	-1
Pour point (^{0}C)	-14	-11	-12
Iodine value g (I_2)/100 g	44.5	43.7	46.3
Sulfur, ppm, max.	34	34	34
Water and sediment, vol%, max.	0	0	0
Copper corrosion, 3 hr at 50°C, max.	№1	№1	№1
Cetane number, min.	41.7	42.3	43.0

Table 4 — Amount of di ($A_{C18:2}$)- and tri ($A_{C18:3}$) unsaturated FAME before and after oxidation, %

	FAME	
	$A_{C18:2}$	$A_{C18:3}$
Before oxidation	54	0.3
After oxidation	16	0

Table 5 — Oxidation stability of diesel and B10 blends

	diesel	B10 FAME	B10 FAME + Bu (5%)	B10 FAME + EO (5%)	B10 FAME + Bu (2.5%) and EO (2.5 %)
Before (OS_{NMR})	9.89	11.28	9.41	16.51	11.34
After (OS_{NMR})	5.88	5.31	7.19	10.07	7.98

want to note, that flashpoints for B10+Bu are decreased up to 86°C.

The cloud and pour points of all B10 blends at the presence of Bu and EO are significantly decreased (up to -12°C).

The amount of sulfur significantly was decreased as the percentage of biodiesel blends from 50 up to 34 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 cetane number, one of the key indicators for diesel fuels, is not significantly decreased in the presence of high-octane number oxygenated components (Table 3).

The oxidation stability of biodiesels was tested by ASTM D 2274-03a and estimated by using NMR data. Amount of $A_{C18:2}$ and $A_{C18:3}$ (di- and tri unsaturated FAME) calculated by literature method[14].

The amount of di- and tri- unsaturated fatty acid methyl ester (FAME) before and after oxidation is 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, high oxidation stability has a FAME+EO B10 fuel blend. Oxidation stability of FAME-Bu and FAME+Bu+EO also is more than that of diesel and B10 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. Despite the oxidation stability of FAME+EO more than FAME+Buand FAME+Bu+EO, its flashpoint and kinematic viscosity are high, 105°C and 3.1 mm^2/s accordingly. Therefore, we consider that the best B10 fuel blend is FAME+Bu with low kinematic viscosity (2.9 mm^2/s), flashpoints temperature (86°C) and high oxidation stability.

As a result of our detailed studying, it can be concluded that *n*-butanol and eucalyptus essential oil can be successfully used in diesel fuels as additivity for improving operational properties.

Generally, we want to note that investigated fuel blends are according to the diesel fuel standards, and suggested blends can be used in diesel engines without any problems.

Conclusion

The exploitation properties of diesel, B100, B10 blends with (or without) n-butanol and eucalyptus essential oil were investigated on the ASTM standards. Obtained results have demonstrated the exploitation accessibility of important fuel properties- such as density, viscosity, amount of sulfur, copper corrosion, flash-, pour- and cloud points for B10 fuels with oxygenated compounds.

Important is to note that the best results demonstrated the FAME+Bu fuel blend.

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