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ORIGINAL PAPER

Biodiesel production from free fatty acids and the effects of its blends with alcohol–diesel on engine characteristics

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Abstract In this experimental study, biodiesel production from free fatty acids of soybean oil and the effects of its blends with alcohol–diesel on diesel engine performance and exhaust emissions were studied. Crude glycerine was neutralized to produce the free fatty acids. Methyl alcohol was reacted with the free fatty acids in the presence of acid catalyst to form biodiesel. Biodiesel, diesel, and alcohols were mixed at different volumetric ratios, and the properties of each blend were determined. The blends and diesel were tested in a single cylinder direct injection diesel engine at full-load conditions. In conclusion, torque and power characteristics of blends were found similar to those of diesel. Break specific fuel consumption of the blends slightly increased depending on lower heating values. CO and smoke emissions decreased up to 34.52 and 39.30 %, respectively. Although NO_x emissions increased with B50, it showed a downward trend with alcohol-containing blends.

Keywords Biodiesel · Esterification · Alcohol · Diesel engine · Exhaust emission

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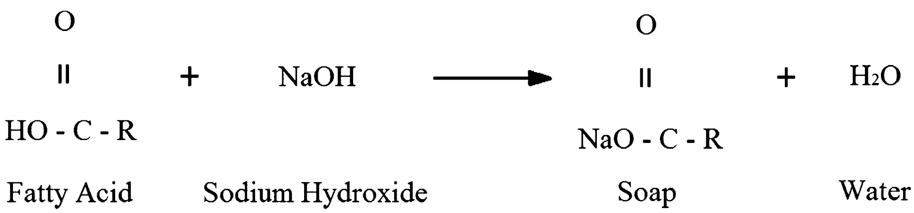
Introduction

Due to environmental concerns and the increase in energy demand, the studies on alternative energy sources have become even more significant day-by-day. Recently, among alternative energy sources, biodiesel as a biomass-based fuel is one of the most frequently focused sources. Biodiesel is a renewable and less polluting alternative energy source for conventional diesel (Resitoglu et al. 2012).

Biodiesel is obtained by reacting vegetable oil or fat with alcohols in the presence of a catalyst. During this reaction called “transesterification,” fatty acids which are the constituents of fat molecules (triglyceride) react with alcohol to form esters (biodiesel). In the biodiesel production process, about 10 % crude glycerine is obtained as by-product (Anastacio et al. 2014). Crude glycerine contains many impurities such as crude glycerine salts, alcohols, saponified fatty acids, and water and does not have any significant economic value. The proportions of impurities in crude glycerine vary depending on the raw material and method used in the production. Crude glycerine purified using methods such as vacuum distillation, adsorption of pollutants on activated carbon, pH adjustment, and solvent extraction can be used in many sectors such as cosmetics, food, and chemical industries and gains economic value (Javani et al. 2012).

During biodiesel production, free fatty acids may form soap as a result of the reaction with catalyst (Gerpen 2005). The saponification reaction is given in Eq. 1. The major part of the saponified free fatty acids is located in crude glycerine and reduces the purity of the glycerine. In case the crude glycerine is neutralized with strong mineral acids, soaps can be converted again into free fatty acids (Singhabhandhu and Tezuka 2010), and the reaction of free fatty acids with high concentrations of alcohol in the presence of acid catalyst forms esters.



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Biodiesel can be used in diesel engines without any modification in pure form or by mixing it with diesel. Biodiesel, which contains about 10 % oxygen by weight, does not contain sulfur and aromatic hydrocarbons, and it has better lubrication property and higher cetane number compared to diesel (Yamin et al. 2013). These superior properties of biodiesel improve combustion efficiency and reduce the pollutant emissions in diesel engine. While biodiesel provide significant reductions in hydrocarbons (HC), carbon monoxide (CO), and soot emissions, it causes a small increase in nitrogen oxide (NO_x) emissions (Chuah et al. 2015).

The use of alcohols is an effective way to improve properties of biodiesel and exhaust emission characteristics of diesel engine. Many studies have been carried out on the use of alcohols such as ethyl alcohol, methyl alcohol, and butyl alcohol with biodiesel. In these studies, alcohols provide advantages such as containing a higher rate of oxygen content, lower viscosity, density, and pour point than biodiesel while they offer disadvantages such as lower cetane number, creating a phase with biodiesel blend, high heat of vaporization, and lower lubricating property.

Alcohols show different effects on diesel engine exhaust emissions depending on its rate in fuels. The blends of alcohols with biodiesel and diesel in a low rate lead to the reductions in HC, CO, NO_x, and soot emissions, while their blends in a high rate cause a further reduction of NO_x and soot emissions, and an increase in CO and HC emissions (Su et al. 2013).

In this study, the biodiesel production from free fatty acids obtained by the neutralization of crude glycerine and the impacts of biodiesel, diesel, and alcohol (ethanol, butyl alcohol, and isopropyl alcohol) blends on diesel engine performance, and exhaust emissions were studied experimentally.

Materials and methods

The crude glycerine was obtained commercially from a facility producing biodiesel from soybean oil. The production of biodiesel in the facility was carried out in 50 min using methyl alcohol and sodium hydroxide as a catalyst (NaOH).

The crude glycerine was neutralized with hydrochloric acid (HCl) by the use of 1 L glass reactor with magnetic stirrer and thermometer. The crude glycerine was heated to 60 °C for rarefaction and HCl was added until pH was 5. The solution was stirred for 30 min, and then the product was allowed to rest on a separatory funnel for phase formation. After the phase formation, free fatty acids were separated from glycerine by means of the separatory funnel. In order to remove the impurities such as alcohol and salt, the free fatty acids were washed with water at 60 °C and dried. During the neutralization process, the conversion of soap in crude glycerine into free fatty acids and salt is given in Eq. 2.

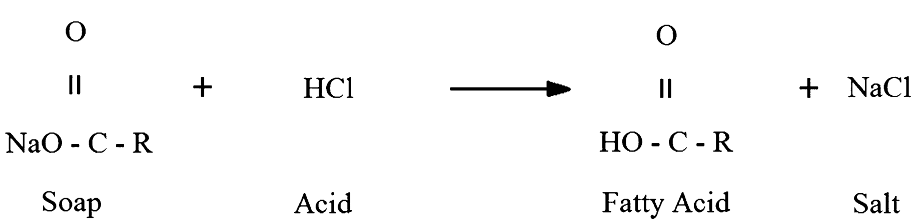

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Figure 1 shows flow diagram of biodiesel production. A 2-L capacity refluxing glass reactor with magnetic stirrer and thermometer was used to obtain biodiesel from free

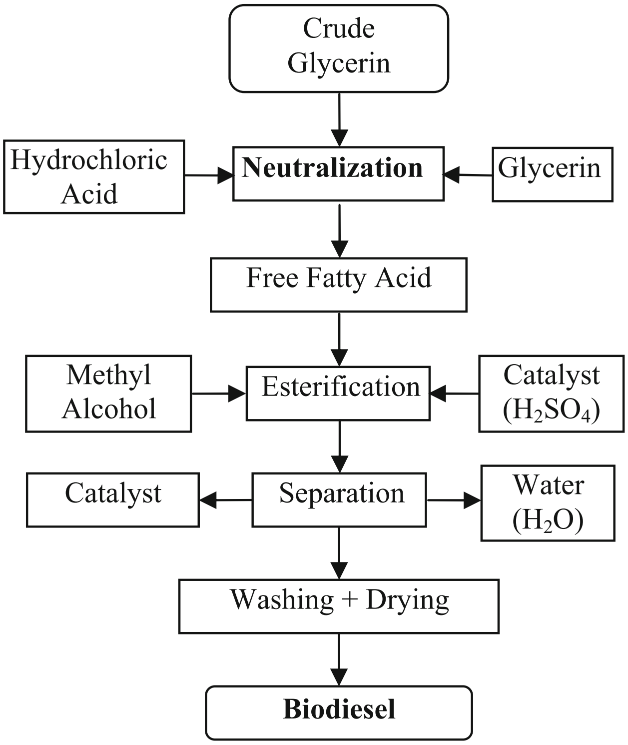


Fig. 1 Flow diagram of biodiesel production process

fatty acids. The reaction was carried out for 3 h at 60 °C using 800 g of free fatty acid, 500 g of methyl alcohol, and 50 g of sulfuric acid (H_2SO_4). After the reaction, solution was allowed to rest in a separatory funnel and it was divided into two phases. The upper phase forms methyl esters (biodiesel), while the lower phase forms the mixture of water, methyl alcohol, and the catalyst (H_2SO_4).

The esters were purified from the catalysts and alcohols by washing with pure water at 65 °C. The production of biodiesel was completed by drying the washed esters at 105 °C. The equation of the esterification reaction is given in Eq. 3.

widespread use and improving effects on fuel properties and engine characteristics. Alcohols were blended with diesel and biodiesel in small quantities as a ratio of 8 % to prevent the adverse effects due to the use with high rates.

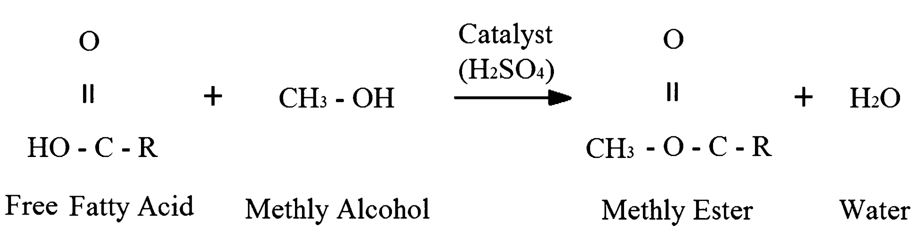
Four different blends were obtained by volumetrically mixing diesel (D), biodiesel (B), ethyl alcohol (E), isopropyl alcohol (I), and butyl alcohol (BU) in the following ratios: %50D + %50B, %42D + %50B + %8E, %42D + %50B + %8I, and %42D + %50B + %8BU. They are named B50, B50E8, B50I8, and B50BU8, respectively. Physical and chemical properties of blends were determined at Cukurova University Fuel Analysis Laboratory.

As shown in Table 1, the properties of blends are similar with the properties of diesel in general. The addition of 8 % ethyl alcohol, 8 % isopropyl alcohol, and 8 % butyl alcohol to B50 led to decreases in cetane number, calorific value, flash point, viscosity, density, and pour point. The flash point of B50 was obtained higher as a rate of 38.93 % than that of diesel. The utilization, transportation, and storage of fuel are provided more safely by the increase of flash point.

The tests of engine performance and exhaust emissions were carried out in a single cylinder, direct-injection Lombardini 4LD 640 diesel engine. Technical specifications of the test engine are given in Table 2.

Each blend and diesel was tested at full-load conditions between 1800 and 3000 rpm with 200 rpm intervals. Before the tests, engine was run for 15 min to reach the operating temperature. The tests were conducted three times for each of the fuels, and the averages of the results were calculated. Schematic view of the experimental setup is shown in Fig. 2.

A hydraulic dynamometer with 0–1000 Nm capacity was used to load the engine. The engine torque and power values were measured using an S-type load cell, while a magnetic pick-up was used to measure the engine rpm. CO and NO_x emission measurements were carried out using



(3)

Biodiesel was blended with diesel and alcohols to improve fuel properties and exhaust emission characteristics of diesel engine. Ethanol, butyl alcohol, and isopropyl alcohol were preferred in blends because of their

Testo 350-S gas analyzer, while soot emission was measured by CAP 3200 emission device. Specifications of gas analyzers and the uncertainties in measurements are given in Tables 3 and 4, respectively.

Table 1 Chemical and physical properties of test fuels

	B50	B50E8	B50I8	B50BU8	EN 14214	D	EN 590
Density (15 °C) (kg/m^3)	0.855	0.851	0.852	854	860–900	0.830	820–845
Viscosity (15 °C) (cSt)	4.1	2.9	2.9	3.0	3.5–5.0	3.3	2.0–4.5
Lower heating value (kJ/kg)	41,520	39,782	40,105	40,397	–	44,149	–
Cetane number	55.315	52.159	52.951	53.086	Min 51	56.415	Min 51
Flash point (°C)	78.5	20	28	42	Min 120	56.5	Min 55
Pour point (°C)	−15	−21	−20	−20	–	−25	–
Copper strip corrosion (3 h, 50 °C)	1	1	1	1	1	1	1

Table 2 Main characteristics of the test engine

Manufacturer/type	Antor Diesel 4 LD 640
Cylinders number	1
Swept volume (cc)	638
Bore (mm)	95
Stroke (mm)	90
Compression ratio	17:1
Maximum speed (rpm)	3000
Maximum power (HP)	13
Maximum brake torque (Nm at 1800 rpm)	43
Injection type	Direct injection
Cooling system	Air-cooled

Results and discussion

Figure 3 shows the performance characteristics of the test engine (torque, power, and break specific fuel consumption). As shown in figure, there has been no significant change characteristically even though torque and power values obtained from blends showed a decreasing trend compared to diesel.

The maximum torque values were measured at 1800 rpm for all test fuels. Compared with diesel, the average reduction rate in torque and power values of B50, B50E8, B50I8, and B50BU8 were 1.70, 2.58, 1.46, and 1.53 %, respectively. The maximum decrease in torque and

Table 4 Uncertainties in measurements

Measurements	Uncertainty ± %
Torque (Nm)	0.27
Power (kW)	0.29
Engine speed (min^{-1})	0.11
BSFC (g/kWh)	0.92
CO (ppm)	2.45
NO_x (ppm)	2.87
Smoke (m^{-1})	2.16

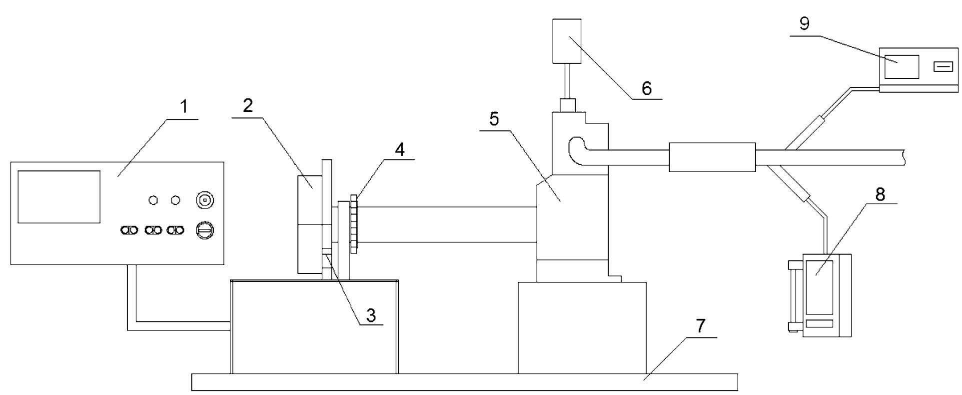


Fig. 2 A schematic view of the experimental setup (*1* control panel, *2* hydraulic dynamometer, *3* S-type load cell, *4* magnetic pick-up, *5* test engine, *6* fuel tank, *7* platform, *8* gas analyze equipment, *9* smoke meter)

Table 3 Specifications of gas analyzers

Equipment		Measuring range	Resolution
CAPELEC CAP3200	*K* value (1/m)	0–10	0.01
Testo 350-S	CO (ppm)	0–10,000	1
	NO_x (ppm)	0–3000	1

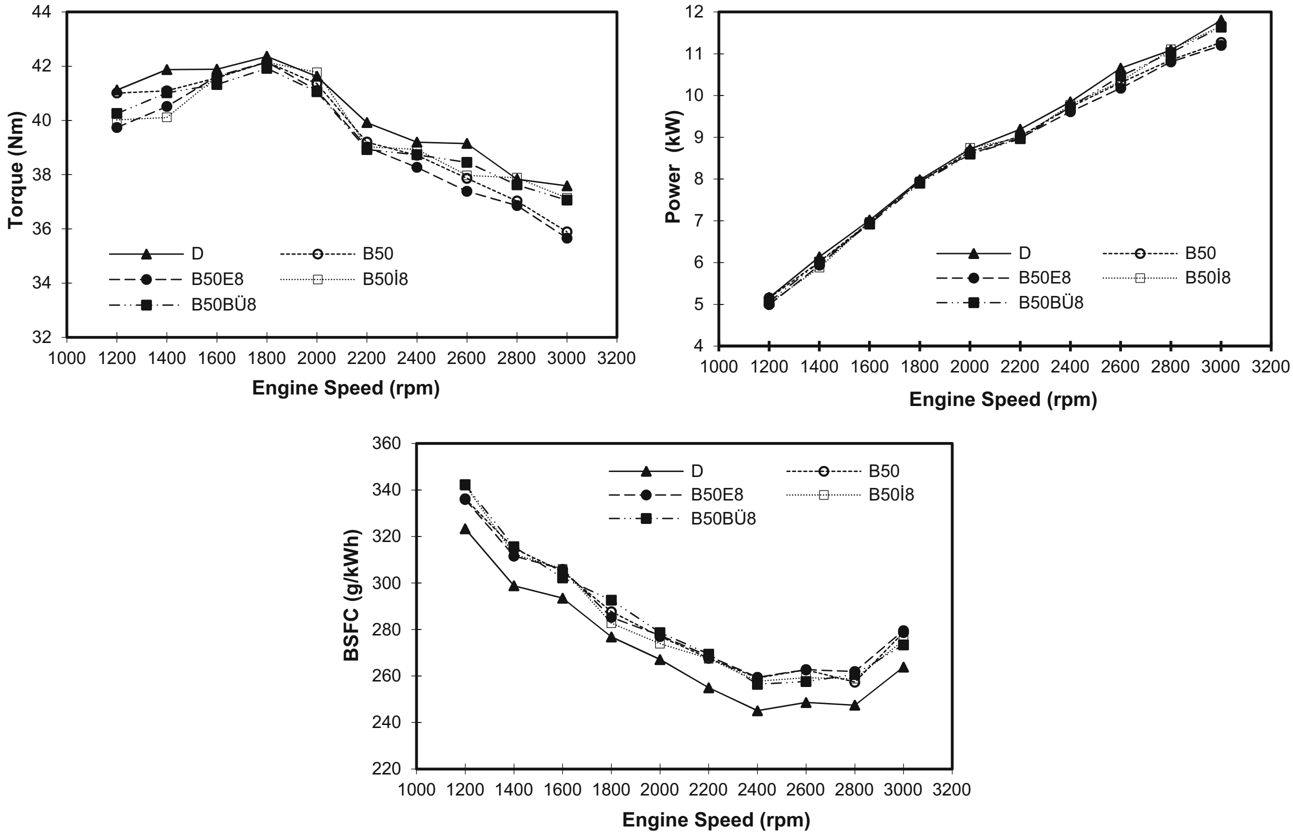


Fig. 3 Performance characteristics of diesel engine at full-load condition

power were obtained as 4.51 % for B50 at 3000 rpm, 5.10 % for B50E8 at 3000 rpm, 4.21 % for B50I8 at 1400 rpm, and 2.10 % for B50BU8 at 1200 rpm. The main reason of the decrease is that blends have a lower calorific value compared to diesel.

Brake-specific fuel consumption (BSFC) values of blends increased compared to diesel due to the low calorific value of blends. The BSFC curve of blends was found parallel to the curve obtained with diesel. Minimum BSFC values were obtained at 2400 rpm for all test fuels. Compared to diesel, maximum increase was obtained as 5.94 % with B50E10 at 3000 rpm. The average increase rates with B50, B50E8, B50I8, and B50BU8 were 4.68, 4.80, 4.26, and 4.74 %, respectively. The average increase rates in BSFC were less than the ratio difference of the calorific value between blends and diesel fuel. This case shows that thermal efficiency of the engine improved with the use of biodiesel and alcohols. This improvement may have resulted from such properties of blends as higher oxygen content, lower viscosity, and lower aromatic hydrocarbon content. These are important fuel properties affecting fuel spray and combustion characteristics.

The emission characteristics (CO, NO_x and smoke emissions) of test engine are shown in Fig. 4. The lowest CO emission values were measured by B50 in general. The CO emission values of the alcohol-containing blends showed an upward trend compared to B50. This stems from the cooling effect that occurs due to the high heat of vaporization when alcohols burn at combustion chamber (Yılmaz and Sanchez 2012). Compared to diesel, there have been substantial decreases in the CO emission values with all blends except B50E8. The average reduction rates obtained from B50, B50I8, and B50BU8 were 22.35, 12.51, and 10.51 %, respectively. The maximum reduction in CO emissions was obtained as 34.52 % with B50 at 2200 rpm.

The NO_x emission of B50 showed an increase especially in high engine speeds compared to diesel. In other respects, mostly lower NO_x emissions were measured with B50E8. In the tests carried out with B50I8 and B50BU8, the measured values were obtained similar to the diesel values. While NO_x emission increased at an average rate of 8.23 % with B50, there has been an average reduction of 5.18 % with B50E8. The maximum NO_x emission was measured as 87 ppm with diesel at 1600 rpm. Due to high heat of vaporization, low cetane number, and low calorific value of alcohols, NO_x values of the alcohol-containing blends decreased compared to B50 and diesel (Siwale et al. 2013).

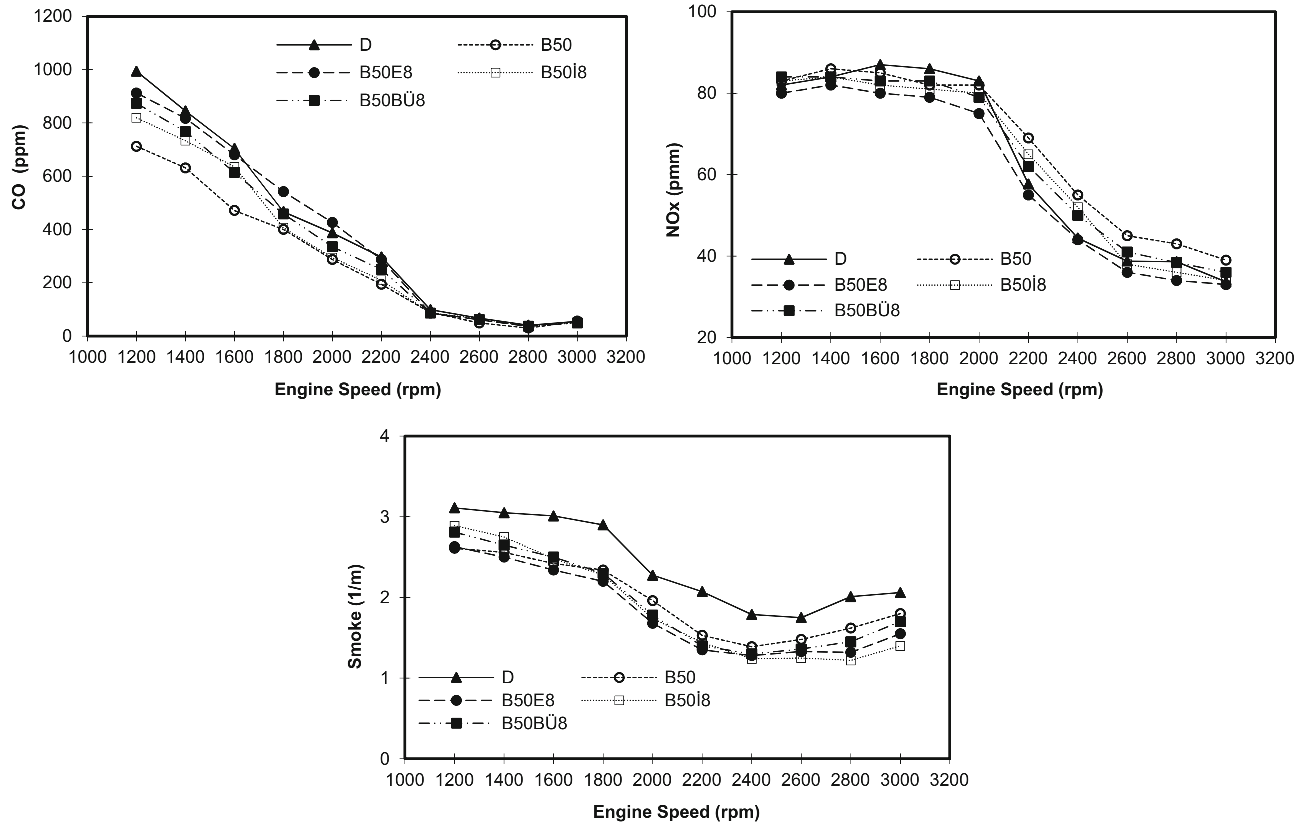


Fig. 4 Emission characteristics of diesel engine at full-load condition

The soot emissions of all blends were measured lower than those of diesel. Maximum reduction rate was 39.30 % at 2800 rpm with B50I8. The average reduction rates obtained with B50, B50E8, B50I8, and B50BU8 were 18.07, 25.23, 24.04, and 20.95 %, respectively. Compared to B50, higher rates of decreases in soot emissions were obtained with alcohol-containing blends. The low viscosity of alcohols improved the spray characteristics and high proportion of oxygen in alcohols increased the efficiency of combustion (Zhu et al. 2013). Herein, alcohol-containing blends showed better performance in reduction of soot emissions.

Conclusion

The properties of blends were similar with those of diesel in general. While alcohol-containing blends provided advantages in terms of lower density, pour point, and viscosity compared with B50, they caused disadvantage in terms of lower cetane number, flashpoint, and calorific value. The torque and power values of blends decreased especially in low and high engine speeds compared to diesel. BSFC showed an increase with blends due to their low calorific values. There have been significant decreases in CO emission with all blends except B50E8 compared to diesel. Compared with B50, alcohol-containing blends led to increases in CO emissions. NO_x emissions were generally measured higher with B50, while it showed a downward trend with alcohol-containing blends. With all blends, lower soot emission was measured compared to diesel. The reduction rates in soot emissions were obtained higher with alcohol-containing blends compared to B50.

References

Anastacio GS, Santos KO, Suarez PAZ, Torres FAG, De Marco JL, Parachin NS (2014) Utilization of glycerin byproduct derived from soybean oil biodiesel as a carbon source for heterologous production in pichia pastoris. Bioresour Technol 152:505–510. doi:10.1016/j.biortech.2013.11.042

Chuah LF, Aziz ARA, Yusup S, Bokhari A, Klemes JJ, Abdullah MZ (2015) Performance and emission of diesel engine fuelled by waste cooking oil methyl ester derived from palm olein using hydrodynamic cavitation. Clean Technol Environ Policy 17:2229–2241. doi:10.1007/s10098-015-0957-2

Gerpen JV (2005) Biodiesel processing and production. Fuel Process Technol 86:1097–1107. doi:10.1016/j.fuproc.2004.11.005

Javani A, Hasheminejad M, Tahvildari K, Tabatabaei M (2012) High quality potassium phosphate production through step-by-step glycerol purification: a strategy to economize biodiesel production. Bioresour Technol 104:788–790. doi:10.1016/j.biortech.2011.09.134

Resitoglu İA, Keskin A, Gürü M (2012) The optimization of the esterification reaction in biodiesel production from trap grease. Energy Sources, Part A 34:1238–1248. doi:10.1080/15567031003792395

Singhabhandhu A, Tezuka T (2010) A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock. Energy 35:2493–2504. doi:10.1016/j.energy.2010.02.047

Siwale L, Kristof L, Adam T, Bereczky A, Mbarawa M (2013) Combustion and emission characteristics of *n*-butanol/diesel fuel blend in a turbo-charged compression ignition engine. Fuel 107:409–418. doi:10.1016/j.fuel.2012.11.083

Su J, Zhu H, Bohac SV (2013) Particulate matter emission comparison from conventional and premixed low temperature combustion with diesel, biodiesel and biodiesel–ethanol fuels. Fuel 113:221–227. doi:10.1016/j.fuel.2013.05.068

Yamin JA, Sakhnini N, Sakhrieh A, Hamdan MA (2013) Environmental and performance study of a 4-stroke CI engine powered with waste oil biodiesel. Sustain Cities Soc 9:32–38. doi:10.1016/j.scs.2013.02.002

Yılmaz N, Sanchez TM (2012) Analysis of operating a diesel engine on biodiesel–ethanol and biodiesel–methanol blends. Energy 46:126–129. doi:10.1016/j.energy.2011.11.062

Zhu L, Cheung CS, Zhang WG, Fang JH, Huang Z (2013) Effects of ethanol–biodiesel blends and diesel oxidation catalyst (doc) on particulate and unregulated emissions. Fuel 113:690–696. doi:10.1016/j.fuel.2013.06.028