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Emission Profile of Rapeseed Methyl Ester and Its Blend in a Diesel Engine

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Abstract

Fatty acid methyl esters, also known as biodiesel, have been shown to have a great deal of potential as petro-diesel substitutes. Biodiesel comprise a renewable alternative energy source, the development of which would clearly reduce global dependence on petroleum, and would also help to reduce air pollution. This paper analyzes the fuel properties of rapeseed biodiesel and its blend with petro-diesel, as well as the emission profiles of a diesel engine on these fuels. Fuels performance studies were conducted in order to acquire comparative data regarding specific fuel consumption and exhaust emissions, including levels of carbon monoxide (CO), carbon dioxide (CO_2), smoke density, and NO_X, in an effort to assess the performance of these biodiesel and blend. The fuel consumption amount of oil operations at high loads was similar or greater than that observed during petro-diesel operation. The use of biodiesel is associated with lower smoke density than would be seen with petro-diesel. However, biodiesel and its blend increased the emission of CO, CO_2, and nitrogen oxides, to a greater degree than was seen with petro-diesel. The above results indicate that rapeseed biodiesel can be partially substituted for petro-diesel under most operating conditions, regarding both performance parameters and exhaust, without any modifications having to be made to the engine.

Index Entries: Biodiesel; engine performance; rapeseed oil; exhaust emission.

Introduction

Biodiesel (fatty acid methyl esters [FAMEs]) is an alternative and renewable energy source, the development of which is hoped to reduce

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global dependence on petroleum, as well as air pollution. Biodiesel derived from diverse vegetable oils and animal fats have been found to exhibit low viscosities, similar to those associated with petro-diesel. Additionally, many of the salient characteristics of biodiesels, most notably volumetric heating value, cetan number, and flash point, are also comparable with those of petro-diesel *(1,2)*. FAMEs, which are derived from vegetable oils and animal fats via alcohol transesterification, are also thought to have great potential as diesel substitutes, and these blends are called biodiesel *(3,4)*. Several processes for the production of biodiesel via acid-, alkali-, and enzyme-catalyzed transesterification reactions have been previously developed *(5,6)*. Transesterification, also called alcoholysis, refers to the displacement of an alcohol from an ester by another alcohol, via a process which is generally similar to hydrolysis. Transesterification occurs through a number of consecutive and reversible reactions. The reaction steps involve the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and then of monoglycerides to glycerol *(7)*.

In general, the applied ratio of FAMEs in mixed biodiesel with petro-diesel ranges between 5 and 30 wt%. Biodiesel has been shown to be compatible with petro-diesel in compression–ignition engines, and mixtures of biodiesel and petro-diesel have been successfully used in engines without any modification. The use of biodiesel would have several advantages over that of petro-diesel, as biodiesel represents both an alternative renewable energy source and a biodegradable nontoxic fuel *(8)*. Biodiesel also carries the advantages of a superior engine combustion emission profile, including low-emission rates. The levels of CO, particulate material, and unburned hydrocarbons (HC), all of which have been proven to exert carcinogenic and mutagenic effects, has been shown to be significantly lower in biodiesel exhaust than in petro-diesel exhaust. Biodiesels can also attenuate the rate of CO_2 recycling in the short-term *(6)*.

Several researchers have observed that the use of biodiesel is associated with a reduction in exhaust emissions. The use of biodiesel in diesel engine has been generally shown to increase nitrogen oxide (NO_x) emissions, and also has been shown to effect a reduction in the HC, CO, and particulate emissions, as compared with petro-diesel. The magnitude of these differences in emission profiles appear to be somewhat dependent on the engine used in the testing *(9)*. The most relevant compositional difference between biodiesel and regular petro-diesel is the oxygen content. Biodiesel contains 10–12% oxygen by weight. However, this high-oxygen content also translates to a lower energy content, which results in reductions in both engine torque and power. However, because biodiesel contains only small amounts of sulphur compounds as in comparison with petro-diesel, biodiesel has also been associated with significant reduced SO_2 emissions *(10,11)*.

In this article, we have attempted to characterize the fuel properties, engine performance, and exhaust emission profiles of rapeseed biodiesel and its blend, using a single cylinder, four-stroke, direct injection (DI), water-cooled diesel engine.

Table 1
Fatty Acid Composition and Characteristics of Rapeseed Oil

Characteristics	Content
Specific gravity	0.917
Moisture content	0.01%
Free fatty acid	0.018%
Unsaponifiable matter	0.39%
Fatty acid % (w/w)	
Palmitic acid ($C_{16:0}$)	5.7%
Stearic acid ($C_{18:0}$)	2.2%
Oleic acid ($C_{18:1}$)	58.5%
Linoleic acid ($C_{18:2}$)	24.5%
Linolenic acid ($C_{18:3}$)	9.1 %

Materials and Methods

Materials

Refined and bleached rapeseed oil was acquired from Onbio Co. Ltd. (Pucheon, Korea). Table 1 shows the fatty acid composition and general characteristics of this rapeseed oil sample. Reference standards of FAMEs, including palmitic, stearic, linolenic, linoleic, and oleic methyl ester (all of >99% purity) were acquired from Sigma-Aldrich Co. Ltd. (St. Louis, MO). The methanol, potassium hydroxide, and other reagents used were of analytical grade.

Transesterification of Rapeseed Oil

The rapeseed oil was transesterified via an alkali process in our laboratory using our developed esterification reaction system as describe below: the heating of the oil, the addition of potassium hydroxide and methyl alcohol, mixture-agitation, glycerol-separation, washing with distilled water, and an additional heating in order to remove remaining water. We used a 30 L reactor system, which was equipped with a mechanical stirrer, a temperature control, electric steam generator, and a condenser. Eighteen liters of rapeseed oil and methyl alcohol were added to the reactor and heated to 50°C with agitation. After a temperature of 50°C was achieved, the prepared potassium hydroxide was dissolved in methanol then rapidly added with stirring, and the reaction continued for an additional 30 min at the same temperature. The reaction was then discontinued, and settled for later separation. Two layers were clearly observed after cooling. The top layer was identified as biodiesel, and the bottom dark denser layer was made up of glycerin. The top layer was then neutralized via the addition of diluted phosphoric acid, distilled with nonreacted methyl alcohol, and finally washed with distilled water.

In our previous report *(6)*, we optimized the production of rapeseed biodiesel via alkali-catalyzed transesterification, using both anhydrous

Table 2
Specification of Test Engine

Item	Specification
Engine model	ND130DIE
Bore × stroke	95 × 95 (mm)
Number of cylinder	1
Displacement	673 (cm^3)
Compression ratio	18
Combustion chamber type	Toroidal
Injection timing	BTDC 23°CA
Injection type	Direct injection
Rated power	13 PS/2400 rpm

methanol and potassium hydroxide. The optimized conditions for alkali-catalyzed transesterification using KOH were found to be as follows: oil to methanol molar ratio, 1:8 to 1:10; catalyst, KOH 1.0% (w/w) by oil weight; reaction temperature, 60°C; and reaction time, 30 min. Under the given conditions, the conversion yield was determined to be approx 98%. From the refined product (rapeseed FAME, and biodiesel), the purity of the product was greater than 99% posttreatment, including washing and centrifugation steps.

Fuel Properties

The fuel properties of biodiesel were assessed in accordance with the test code developed by the Korean Petroleum Quality Inspection Institute (Gwangju, Korea). We assessed the properties of the pure biodiesel (BDF 100), as well as a blend of petro-diesel with 20% biodiesel by volume (BDF 20).

Emissions and Engine Performance

Both the rapeseed biodiesel (BDF 100) and its blend (BDF 20) were tested in a single cylinder, four-stroke, DI, water-cooled diesel engine, with a rated output of 13 PS at 2400 rpm and a compression ratio of 18:1. The details are provided in Table 2. A schematic diagram of the experimental apparatus used to measure the performance and emissions from the engine are shown in Fig. 1. Engine performance and emissions were determined at different engine loads (0, 25, 50, 75, 90, and 100% of the load corresponding to the load at maximum power) at engine speeds ranging from 1000 to 2000 rpm (Table 3). After the engine reached a stabilized condition, emissions including smoke, CO, CO_2, and NO_x, were measured with a smoke meter (Hesbon, HBN-1500, Korea), and an online exhaust gas analyzer (Motor branch, Mod. 588), and were then recorded

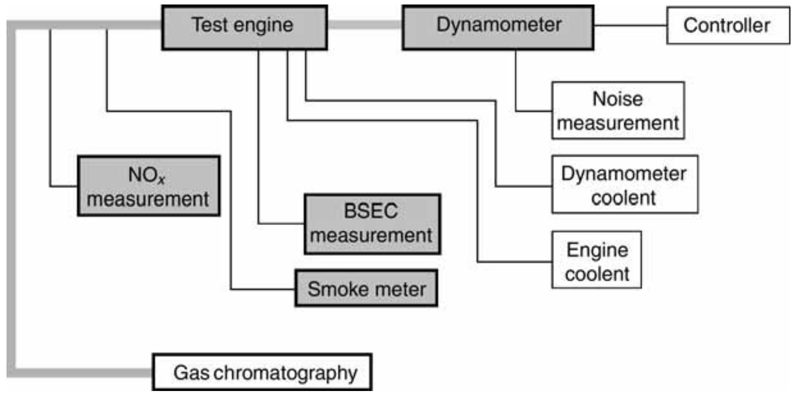

Fig. 1. Schematic diagram of experimental apparatus.

Table 3
Engine Test Condition of Petro-Diesel, Biodiesel, and Its Blend

Fuel	Engine speed (rpm)	Engine load (%)
Petro-diesel	1000	0
BDF 20	1300	25
BDF 100	1500	50
	1700	75
	2000	90
		100

at different engine loads and speeds. Each of these readings was replicated twice in order to acquire reasonable values. Parameters including engine speed, torque, and fuel consumption were also assessed, and from these values, brake power and brake-specific fuel consumption (BSFC) were computed.

Results and Discussion

Fuel Preparation and Its Characteristics

In order to conduct the alkali-catalyzed transesterification process with the rapeseed oil, we applied several different reaction systems. In the alkali-catalyzed transesterification, the amounts of free fatty acid were proposed to be below 0.5% on the basis of oil weight, to ensure a high conversion yield *(12)*.

Figure 2 depicts the time-course of rapeseed oil transesterification at a 1% catalyst concentration (w/w), a molar ratio of 1:6, and a temperature of 60°C. Within the first 5 min, the reaction proceeded quite rapidly. Rapeseed oil was converted to greater than 86% within the first 5 min, and

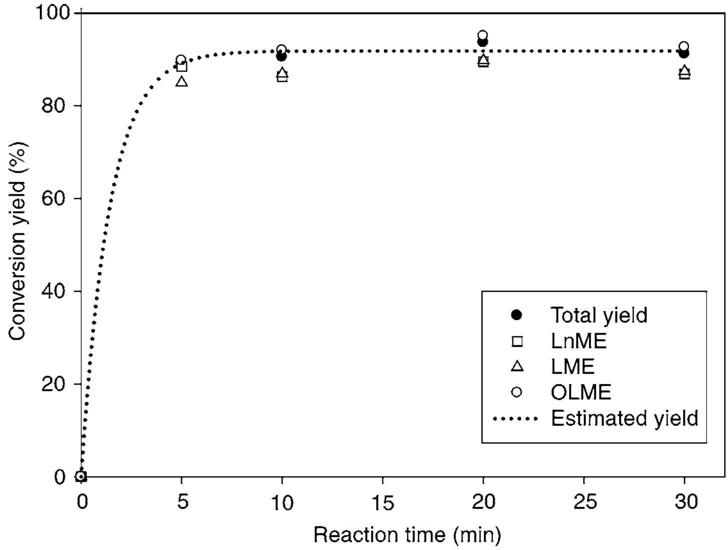

Fig. 2. Time-course of rapeseed oil transesterification on 60ºC, 1:6, 1% potassium hydroxide and 600 rpm in 30 L reactor.

conversion reached an equilibrium state after approx 10 min. At a reaction time of 30 min, linolenic and linoleic acid methyl ester were generated at low-conversion rates, whereas oleic methyl ester was produced fairly rapidly. After transesterification under optimal operation conditions, the rapeseed methyl ester changed in color from yellow to brownish-yellow, and, on average, an identical amount of biodiesel was acquired from 18 L of rapeseed oil. The properties of biodiesel and its blend are shown in Table 4. The kinematic viscosity of rapeseed oil was determined to be higher than that of petro-diesel at a temperature of 40°C. After reaction, the kinematic viscosity dropped, becoming lower than that of the prepared rapeseed oil. It was further reduced with an increase in the amount of petro-diesel in the blend. We also observed a similar reduction in specific gravity. The flash points of both the biodiesel and the blend were higher than 100°C, which has been determined to be safe for both storage and handling. Ash, sulfur, cloud point, acid value, water content, and cetan number were adjusted to quality standard.

Engine Performance

The term "brake-specific" refers to quantities which have been normalized by dividing by the engine's power. Therefore, the BSFC is equal to the fuel-flow rate, divided by the power of the engine *(13)*. It has been reported that the increase in the BSFC can be attributed principally to the lower energy content of the blended fuel *(14)*.

The BSFC values of each fuel, according to changes in the speed of the engine, are shown in Fig. 3. At the tested engine speeds, the increases in

Table 4
Fuel Properties of Rapeseed Biodiesel and Its Blend

Property	Standard	BDF 100	Standard	BDF 20	Test method
Flash point (PM, °C)	min. 100	182–186	min. 40	59	KS M2010-99
90% Distillation temp. (°C)	max. 360	–	max. 360	347	ASTM D86
10% Ramsbotton carbon residue (wt%)	max. 0.5	–	max. 0.15	0.05	ASTM D4530
Ash (wt%)	max. 0.01	max. 0.01	max. 0.02	max. 0.01	KS M2044-00
Sulfur (wt%)	max. 0.02	0.01–0.004	max. 0.043	0.019	KS M2027-98
Kinematic viscosity (40°C, cSt)	min. 1.9 max. 6.0	4.519–4.570	min. 1.9 max. 5.5	3.316	KS M2014-99
Copper strip corrosion (100°C, 3 h)	max. 1	1	max. 1	1	KS M2018-97
Cetan number	min. 49	–	min. 45	51	KS M2610-01
Water and sediment (vol%)	max. 0.05	max. 0.01	–	–	KS M2115-96
Density (15°C, kg/m^3)	–	–	min. 815 max. 855	852.4	KS M2002-01
Cloud point (°C)	–	–	min. 0.0	–17.5	KS M2016-96
Acid value (mg KOH/g)	max. 0.80	0.20	–	–	KS M2004-00

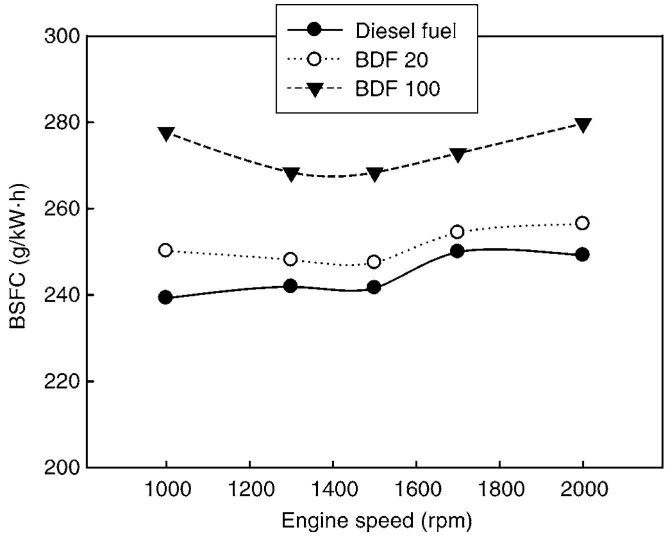

Fig. 3. Variation of brake-specific fuel consumption with engine speed for different fuels tested.

the amount of BDF in the fuel blend evidenced a consistently increasing trend in the BSFC. Variations in the BSFC values according to differences in the biodiesel content of the fuels were found to exhibit a trend similar to that associated with engine speed. In the case of petro-diesel, increases in the speed of the engine were associated with increases in the rate of fuel consumption. BDF 20, which contained 80% petro-diesel, also evidenced a trend similar to that of petro-diesel. In the case of BDF 100, we noted low-BSFC values at 1300–1500 rpm, in comparison with those of the other tested engine speeds. At an average speed of 1300 rpm, the BSFC values for BDF 20 and BDF 100 were determined to be 2.6–10.9% higher than those of petro-diesel. This trend was observed owing to the fact that ester has a lower heating value (lower calorific value) than does petro-diesel, and thus more FAME-based fuel is required for the maintenance of a constant power out put *(13)*.

Emission Studies

Figure 4 shows variations in the density of smoke generated during the tests of the different fuels (petro-diesel, BDF 100, and BDF 20) and engine speeds (1000–2000 rpm). Under engine load <75% conditions, the emitted smoke percentage was low, without relation to the tested fuels or engine speed parameters. At an engine load of >75%, increases in BDF content resulted in markedly lower smoke emission. Under high speed and engine load conditions, smoke emission from the BDF 100 and BDF 20 fuels were lower than those observed with the regular petro-diesel. Smoke was determined to decrease consistently for all of the tested engine conditions,

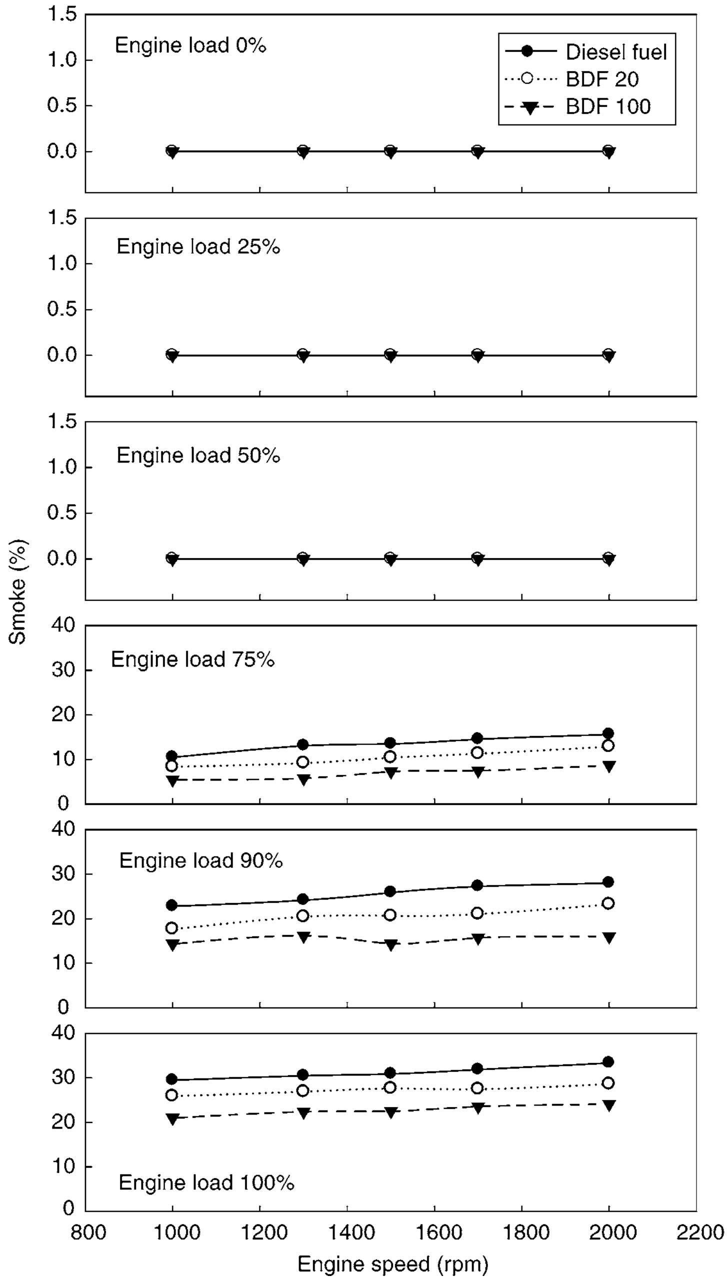

Fig. 4. Variation of smoke density with load for different fuels tested.

along with increases in the amount of biodiesel in the fuel blend. In particular, BDF 100 was associated with a 26.05–28.73% reduction in smoke production in comparison with that of the petro-diesel. Because of the heterogeneous nature of petro-diesel combustion, fuel/air ratios, which affect smoke formation, tend to vary within the cylinder of a diesel engine.

Smoke formation occurs primarily in the fuel-rich zone of the cylinder, at high temperatures and pressures. If the applied fuel is partially oxygenated, locally over-rich regions can be reduced and primary smoke formation can be limited *(13)*.

Nitric oxide (NO) and nitrogen dioxide (NO_2) are usually combined together as NO_x *(9)*. Variations in NO_x emissions according to engine load and speed with the different tested fuels (petro-diesel, BDF 100, and BDF 20) are shown in Fig. 5. Under nonengine load conditions, NO_x emissions were measured to be approx 200 ppm with the BDF 20 and BDF 100, but the petro-diesel did not emit NO_x at any of the tested engine speed ranges. NO_x emissions trended higher directly with increases in the engine load for all of the tested fuels, and were also observed to increase directly with biodiesel content. However, the tested engine speeds did not affect NO_x emission significantly. Regarding biodiesel blends, we noted no significant differences across the range of engine load tested in our study. The NO_x emissions associated with the blends were found to be slightly higher than those of the regular petro-diesel, under both full and partial loads.

The reasons behind these observed increases in NO_x emission remain poorly understood. NO_x emissions have been reported by several researchers to be increased along with the use of biodiesel. Three principal factors affect the emission of NO_x as the result of combustion: oxygen concentration, combustion temperature, and time. The observed NO_x emission increases appeared to have been induced as the result of increases in the temperature of the combustion chamber, which were apparently the result of the 10% oxygen content of the biodiesel *(13,14)*. However, some other studies have reported that NO_x emissions also exhibit a decreasing trend. When operated with pure coconut oil, NO_x emissions were reduced by approx 40% *(14)*.

The variances in CO emissions that resulted from the changes in injection timing, fuel type, and load were found to be significant *(9)*. The emission profiles of CO when running the diesel engine on blends—from BDF 20 to BDF 100—were compared with those associated with petro-diesel, as shown in Fig. 6. CO emissions were determined to be relatively higher in the case of BDF 20 and BDF 100 than with petro-diesel. Under nonload conditions, BDF 100 was determined to emit a greater quantity of CO than did petro-diesel, across the engine speed continuum. However, under full-load conditions, CO emissions increased directly with biodiesel contents at low engine speeds. Also, increases in the engine speed occurred concomitantly with diminutions in the degree to which CO was emitted. Increases in the engine load resulted in greater CO emission. It is generally accepted that the presence of oxygen in the fuel, which facilitates the combustion processes, also results in a reduction of exhaust CO emission, as compared with petro-diesel *(13)*.

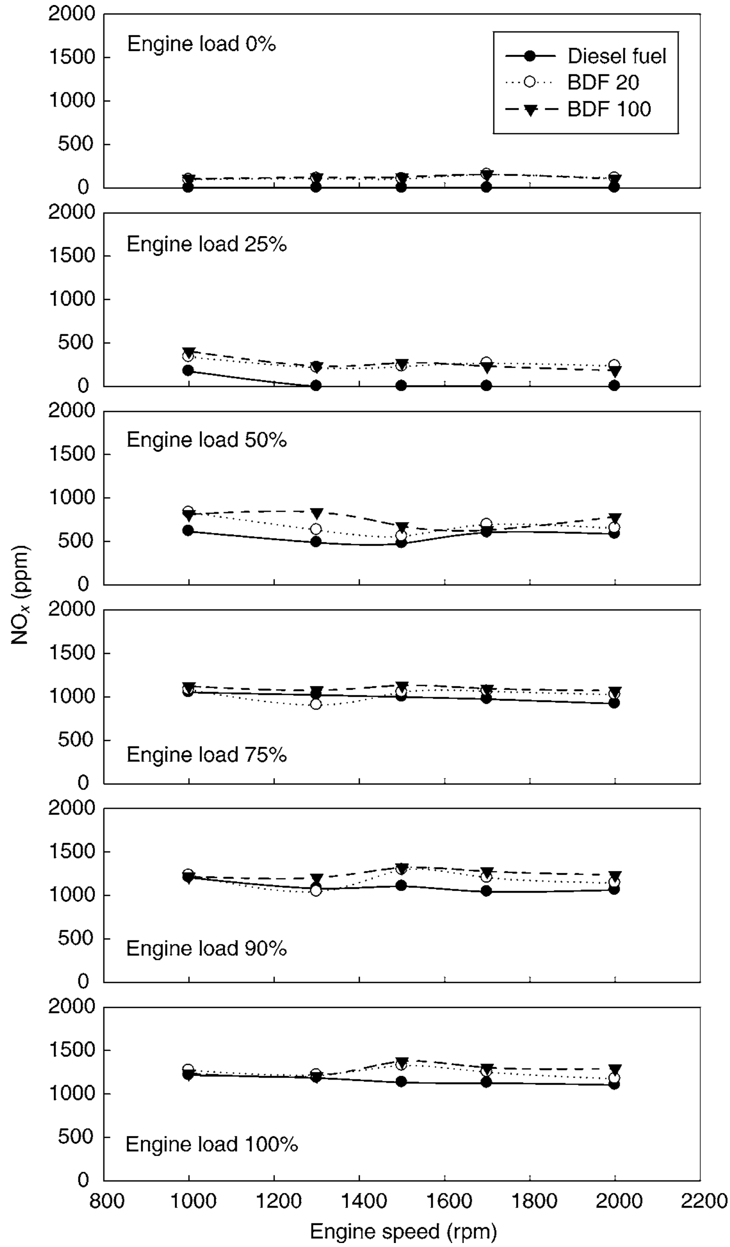

Fig. 5. Nitrogen oxides emission vs engine speed at various engine loads.

Figure 7 profiles CO_2 emissions detected as the result of the operation of a diesel engine running on BDF 20 to BDF 100 and petro-diesel. CO_2 emissions were determined to be relatively high in the case of BDF 20 and BDF 100. Under nonload conditions, BDF 100 emitted a greater quantity of CO_2 than did petro-diesel at all engine speeds, in contrast to the low smoke

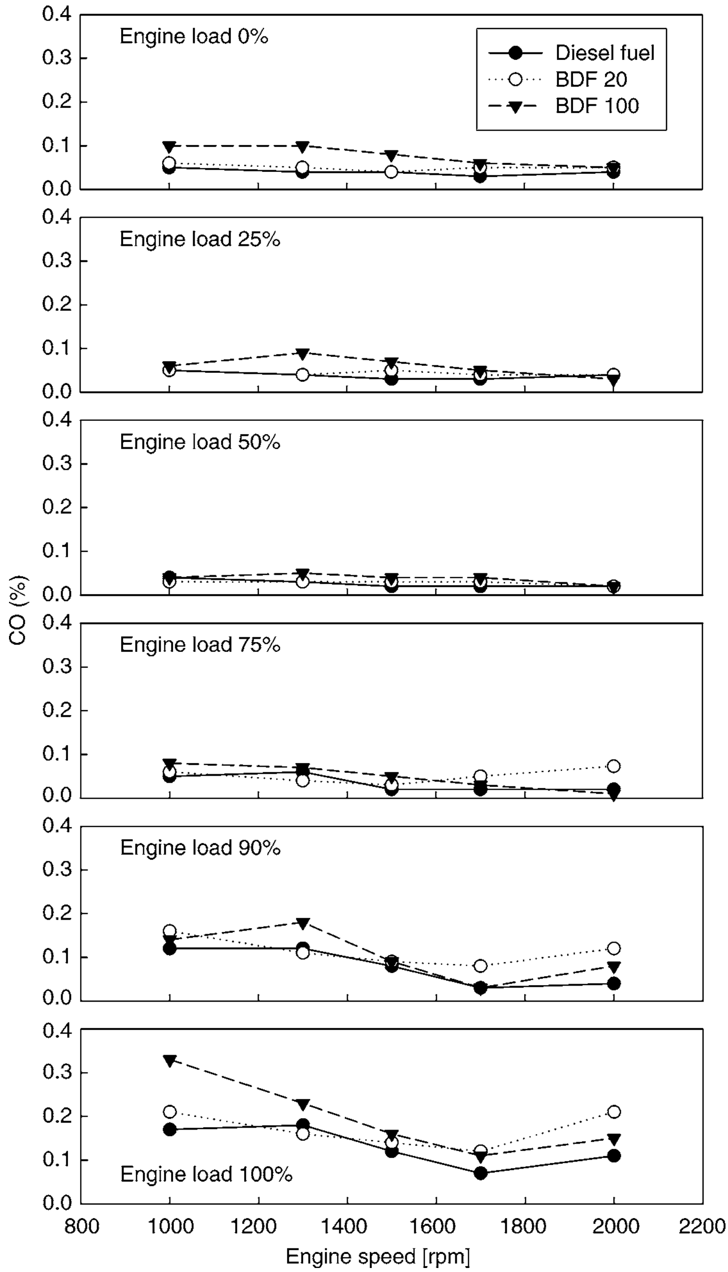

Fig. 6. Carbon monoxide emission vs engine speed at various engine loads.

density detected under such conditions. Under full-load conditions, CO_2 emissions did not vary with biodiesel content at low engine speeds. Also, increases in the engine speed were associated with increases in the emission of CO_2. In general, increases in the engine load were associated with a greater degree of CO_2 emission, whereas engine speed did not affect emission rates.

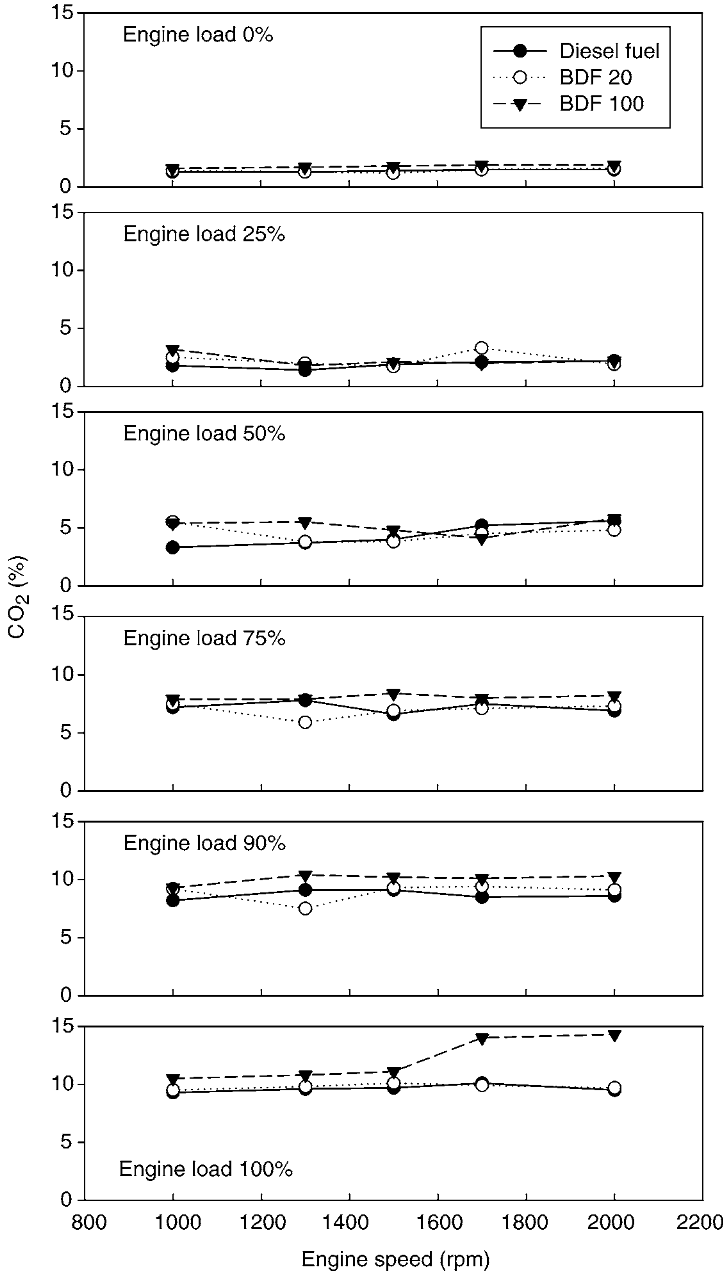

Fig. 7. Carbon dioxide emission vs engine speed at various engine loads.

Conclusions

Biodiesel is a fatty acid alkyl ester, and can be derived from any vegetable oil via transesterification. Biodiesel is a renewable, biodegradable, and nontoxic fuel. Here, we transesterified rapeseed oil with methanol in the presence of alkali, and the biodiesel which was obtained was then investigated regarding its fuel properties and exhaust emission profile.

All of the results which were obtained for the rapeseed biodiesel have been compared with those of petro-diesel. The following conclusions may be drawn from this study:

1. The physiochemical properties and engine performance of rapeseed biodiesel are comparable to those of petro-diesel.
2. The fuel consumption of biodiesel and its blends at high loads was similar or greater than that observed during petro-diesel operation.
3. The use of biodiesel is associated with lower smoke density than would be seen with petro-diesel. However, biodiesel and its blend slightly increased the emission of CO, CO_2, and nitrogen oxides, to a greater degree than was seen with petro-diesel.

The findings in this article, when taken together, indicate that rapeseed biodiesel can be partially substituted for petro-diesel under most operating conditions, regarding both performance parameters and exhaust, without any modifications having to be made to the engine. However, it is suggested that subsequent studies be conducted to elucidate the improvement of diesel engine for the useful application of biodiesel and its blends.

Acknowledgments

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