African Journal of Biotechnology Vol. 10(72), pp. 16300-16313, 16 November, 2011
Available online at http://www.academicjournals.org/AJB
DOI: 10.5897/AJB11.138

Full Length Research Paper

Exhaust emissions and combustion performances of ethylene glycol monomethyl ether palm oil monoester as a novel biodiesel

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Accepted 14 October, 2011

A novel biodiesel named ethylene glycol monomethyl ether palm oil monoester was developed. This fuel owns one more ester group than the traditional biodiesel. The fuel was synthesized and structurally identified through FT-IR, P1PH NMR analyses and GPC. Engine test results showed that when a tested diesel engine was fueled with this biodiesel in the place of 0# diesel fuel, engine-out smoke emissions decreased by 69.0 to 89.3%, and nitric oxide (NOx) also lessened significantly, but unburned hydrocarbon (HC) and carbon monoxide (CO) emissions generally do not change noticeably compared with pure diesel fuel. In the area of combustion performances, both engine in-cylinder pressure and its changing rate with crankshaft angle were increased to some extent for ethylene glycol monomethyl ether palm oil monoester because of the higher cetane number and shorter ignition delay. Due to certain amount of oxygen contained in the new biodiesel resulting in the low calorific value, the engine thermal efficiency dropped by 14.4% at record level when fueled with the biodiesel, which needs to be improved in the future.

Key words: Biodiesel, ethylene glycol monomethyl ether palm oil monoester, engine-out emissions, combustion.

INTRODUCTION

In recent years, growing awareness of the complete depletion of petroleum oil in the near future and serious atmospheric pollution caused by automobile industry has inspired much research for clean alternative fuels to substitute for fossil fuels (Crooles, 2006; Pugazhvadivu and Jeyachandran, 2005; Kaplan et al., 2006). One of the most promising alternative energy sources is biodiesel. Biodiesel contains significantly less sulfur and nitrogen, which makes the fuel more environment-friendly than petroleum fuels. Because it is renewable and available worldwide, it has a bright future for practical application.

A traditional biodiesel was used to be the methyl ester of vegetable oil, which is prepared through trans-esterification of vegetable oils with alcohol. Many studies show that such biodiesel, containing certain amount of oxygen, can lead to remarkable reduction in diesel engine exhaust emissions (Usta et al., 2005; Lapuerta et al., 2005; Cetinkaya and Karaosmanoglu, 2007). Thus, it has been called a green fuel for diesel engine. However, since there is only one ester group (two oxygen atoms existing in each monoester molecule), the oxygen content in traditional biodiesel is at a comparatively lower level, so the reduction in emissions is not just as significant as anticipated when diesel engine burns it or its mixture with diesel fuel. Experiments have shown that the reduction rate in engine-out smoke emissions is correlated with the content of oxygen of the fuel.

Therefore, to enhance the effect of traditional biodiesel in reducing engine-out smoke formation, the introduction of other ether group into its molecule was attempted. As

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Abbreviations: NOx, Nitric oxide; **HC,** hydrocarbon; **CO,** carbon monoxide, **FT-IR; P1PH NMR; GPC, BMEP.**

Table 1. Specification of the used chemicals.

Chemical	Density (kg/m^3)	Boiling point (°C)	Molecular weight	Standard
Palm Oil	917 ~ 944	-	-	Primes state
Ethylene glycol monomethyl ether	965.0	134	76.10	Analytically pure
Ethanol absolute	789 ~ 791	78	46.07	Analytically pure
Potassa	950	-	23.5	Chemically pure

(–OH) Absorption peak in the region of 3200~3600 cm^{-1} indicating that there was little fatty acid and ethanol in the treated palm oil (Figure 1).

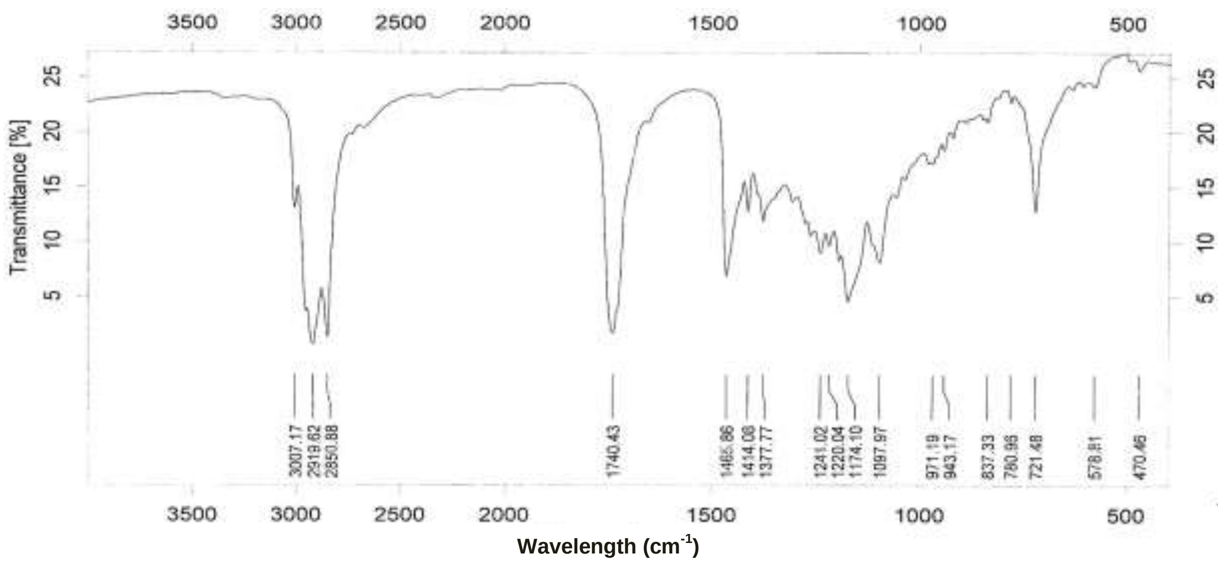


Figure 1. infrared spectrogram of palm oil after treatment.

is well known, palm oil comes from oil palm which is one of the plants with the highest rates of oil productivity, and it can be divided into RBD PO and RBD PKO extensively used for food. Hence, a novel biodiesel, ethylene glycol monomethyl ether palm oil monoester has been synthesized in this paper, which was also studied on the performance in reducing engine-out exhaust emissions and combustion.

MATERIALS AND METHODS

Preparation of palm oil monoester

The new palm oil monoester was synthesized with a commercially refined palm oil and ethylene glycol monomethyl ether as reactants (Table 1). Initially, the selected palm oil was treated through extraction with ethanol as solvent at a temperature of 90°C to remove tiny amount of organic fatty acid of about 0.35 mg KOH/g in it, and was then purified under vacuum condition. FT-IR analysis justified that there was no vibration (Figure 1).

The subsequent transesterification reaction was carried out in a flask with the acid-free palm oil of 600 ml and ethylene glycol monomethyl ether of 210 ml at a temperature of 80°C using 0.6% KOH as catalyst. Upon completion of the reaction which lasted for approximately 0.5 h, the crude product was first neutralized with diluted HCl solution and then separated from the water phase. Subsequently, it was purified in a vacuum to remove ethylene glycol monomethyl ether left over in the ester phase after 12 h. Finally, it was dried using $CaCl_2$ agent, and the yield of palm oil monoester in laboratory can was close to 85%.

Structure analysis

The chemical structure analysis of the new palm oil monoester was conducted with FT-IR, P^{1P}H NMR and GPC analytical techniques (Davies and Henrissat, 1995; Yuan et al., 2008). The test conditions were also confirmed (Table 4 and Figure 3).

FT-IR analysis was performed on an EQUINOX55 FT-IR spectrometer whose sample cell is KBr crystal. A superconducting NMR spectrometer of INOVA type made by VARIAN Company was employed to accomplish P^{1P}H NMR analysis. CDClB$_{3B}$ was selected as a solvent, and TMC as a standard reference. The spectrometer operating frequency was 400 MHz. The Gel permeation chromatography (GPC) 515-2410 system came from American Water Company including 515 HPLC pump, 717 auto sample, 2410 refractive index detector, millennium 32 and styragel (HR2_HR3_HR4E). The experimental condition involved THF as

Table 2. Specification of DI diesel engine utilized.

Parameter	Magnitude	Parameter	Magnitude
Bore	100 mm	Rated speed	2300 rpm
Stroke	115 mm	Rated power	11 kw
Connecting rod length	190 cm	Combustion chamber	ω shape
Displacement	0.903 L	Compression ratio	18

For comparison study, 0# diesel fuel meeting China national technical specification was utilized and named B0. In the mean time, it was mixed with the palm oil monoester (B100) in a volume proportion of 3:1(B50) and 1:1(B25) to investigate the effect of the mixtures on engine-out exhaust emissions and combustion performances.

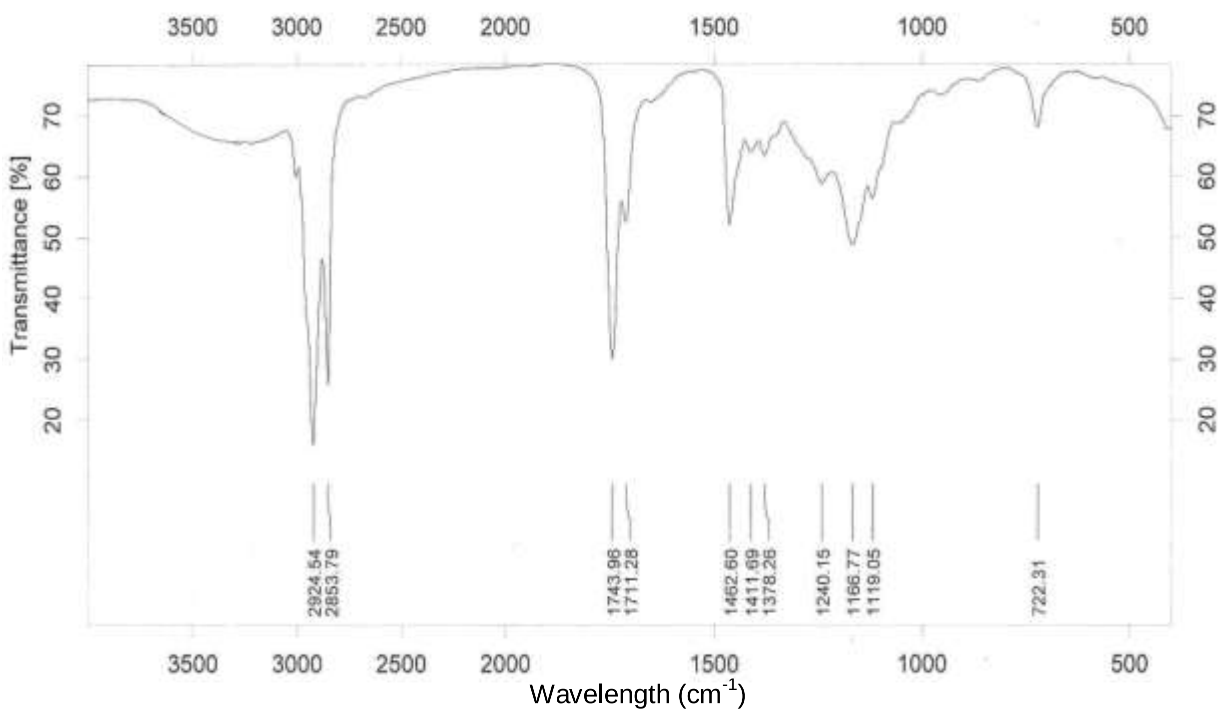


Figure 2. IR spectrum of palm oil monoester.

mobile phase, velocity of 1 ml/min and temperature detector below 40°C.

Engine test

A single cylinder, four-stroke, water-cooled, DI diesel engine was adapted to complete determination of exhaust emissions and combustion performances. The technical parameters of the engine are tabulated in Table 2. An AVL DiSmoke 4000 smoke opacity indicator was used to record smoke intensity in extinction coefficient, and an on-line exhaust emission analyzer was utilized to examine CO, HC and NOx emitted. An angle calibration apparatus and a pressure transducer of Kistler type were used to pick up crankshaft angle and in-cylinder pressure. A CS22000 data gathering and analyzing system was utilized to process data.

The engine tests were carried out under the following conditions: Ambient temperature of 23°C, humidity of 86%, and engine water-cooling temperature of 95°C. In the experiment, when the engine approached a stable operation at a fixed steady state, all kinds of determinations were made according to certain well-defined procedures.

RESULTS AND DISCUSSION

Chemical structure

Figure 2 and Table 3 list the main absorption frequencies displayed in IR spectrum obtained for the new palm oil monoester. No absorption peaks above 3100 cm^{-1} was found, implying that there is no hydroxyl group (-OH) in the synthesized product. Hence, it was easily confirmed that the product is an ester involving ether group.

GPC can help to detect simultaneously the content of diglycerides, triglycerides, glycerol and fatty acid methyl

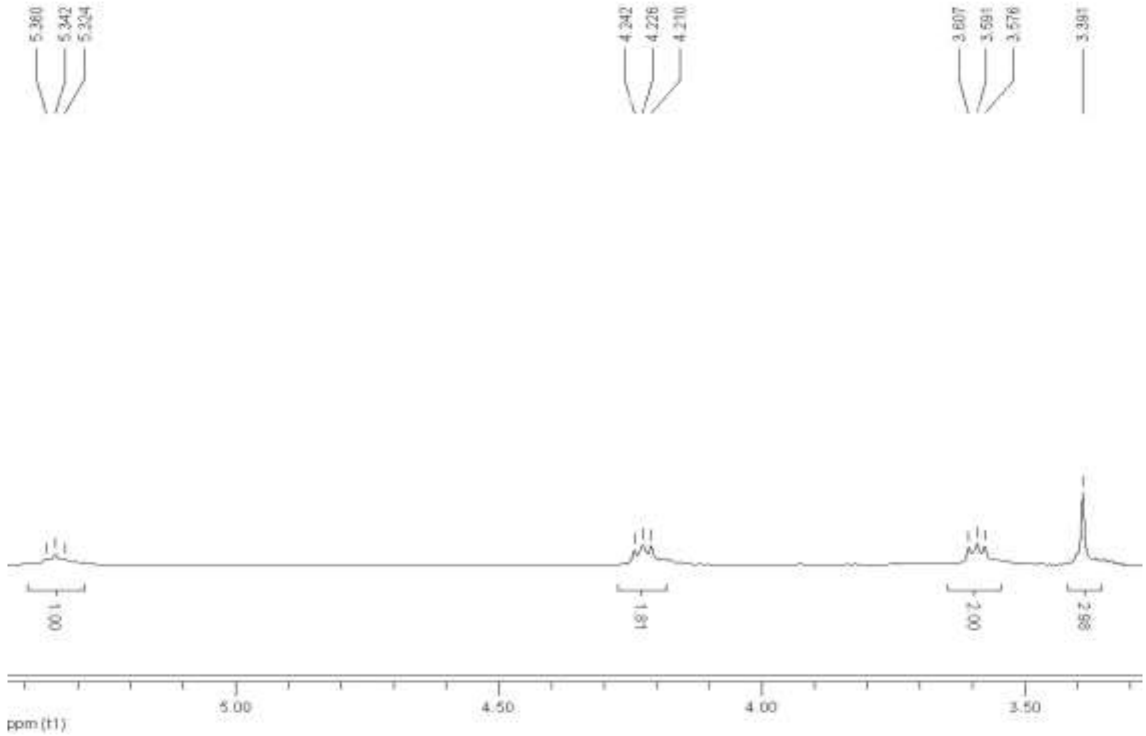


Figure 3. P^{1P}H NMR wave spectrogram of palm oil monoester.

Table 3. FT-IR spectrum data of palm oil monoester.

Frequency (cm^{-1})	Group attribution	Vibration type	Strength
2924.52	-CHB$_{3B}$, -CHB$_{2B}$	νB$_{asB}$	s
2853.79	-CHB$_{3B}$, -CHB$_{2B}$	νB$_{sB}$	s
1743.96	C=O	ν	s
1462.60	-CHB$_{2B}$	δ	m
1378.26	-CHB$_{3B}$	δ	m
1166.77	C-O-C	νB$_{asB}$	m
1119.05	C-O-C	νB$_{sB}$	m
722.31	$(CH_2)n$ (n>4)	-	w

Figure 3 and Table 4 illustrates P^{1P}H NMR data gained for the palm oil monoester. Chemical shift 5.342 ppm belongs to the protons attached to C=C group in the molecules, while chemical shift 4.226, 3.591 and 3.391 ppm, respectively belonged to the protons existing in the group $-COOCH_2CH_2OCH_3$ in the order from the left to the right. More peaks occurring in the

ester in the process of transesterification reaction with a refractive index detector. Table 5 illustrates that the main component of palm oil is fatty acid glycerin ester whose number average molecular weight mainly distributes in 1426 or so, which is consistent with the known composition of palm oil. After transesterification, the peak of fatty acid ester (Mw 1426) almost disappeared, which meant that fatty acid glycerides have been transformed into fatty acid ether ester (biodiesel) thoroughly, while the peak of number average molecular weight of 566 has correspondingly appeared.

Exhaust emissions

Two types of engine operation modes running at 1600 and 2200 rpm, respectively were selected to study the changes of exhaust emissions under different partial brake mean effective pressures (BMEP). Figure 4 displays the effects of the new palm oil monoester on

Table 4. $P^{1P}H$ NMR data of palm oil monoester.

Chemical shift (ppm)	Proton peak splitting	Coupling constant (Hz)	Peak area/proton number
5.342	Triplet	6.4	1.281/-
4.226	Triplet	3.6	1.81/2
3.591	Triplet	3.6	2.00/2
3.391	Singlet	-	2.98/3
<3.000	More	-	more

Chemical shift region below 3.000 ppm are all attributed to protons in the fatty groups (-R) and other non-fatty ester compounds. Therefore, the chemical structure of the new prepared biodiesel was easily confirmed as $RCOOC^1H_2C^2H_2OC^3H_3$.

Table 5. GPC data of palm oil monoester.

Peak		Mn	MP	RT (min)	Area (mv.s)	Peak area (%)
	I	2713	2649	23.02	3.81	0.10
Palm oil	II	1426	1382	23.80	393.05	99.47
	III	1005	1029	26.25	16.96	0.43
	I	1504	1481	24.33	77.56	0.49
Palm oil monoester	II	1120	1128	24.97	725.27	4.60
	III	566	562	25.99	14969	94.85
	IV	230	236	28.41	10.57	0.06

engine-out smoke emissions at 1600 and 2200 rpm, respectively and it is very clear that a considerable decrease has been approached. When the engine burnt the B25 under partial loads at 1600 rpm, there was a relative reduction in smoke emissions by 26.2 to 52.4%. Within the same tested partial load range, the decrease by 51.9 to 71.4% was also obtained for B50. At 2200 rpm, reductions by 12.8 to 27.8% and by 51.6 to 74.1% were reached, respectively for the two mixtures within the tested partial load range. After burning B100, the reduction by 69.0 to 81.0% and by 83.3 to 89.3% in smoke emissions was observed at two different partial loads, whose effect was more obvious. As a kind of oxygenated fuel (more than 10% oxygen), the molecule of biodiesel does not contain aromatic, and the ratio between hydro and carbon (C/H) is far less than the saturated hydrocarbon. Because smoke is mainly generated in the diffusion combustion, oxygen capacity can improve the issue of local hypoxia, so the accession of biodiesel can increase premixed combustion and decrease diffusion combustion in areas of high concentration of fuel especially.

Furthermore, Figure 5 presents test results of CO emissions under different BMEP at the speed of 1600 and 2200 rpm. The figure reveals that at the low load, CO emission does not change significantly, as well as with increasing of loads, CO emissions also increased rapidly. When the BMEP was low, the engine was working at oil-poor state. Due to the excessive amount of air, fuel can be more completely combusted, and thus CO emissions remain at a stably low level. As the biodiesel increased in content of fuel, CO emissions also rapidly increased under the high load. Because of the low calorific value of biodiesel and the low temperature in cylinder under the high load, combustion was not sufficient. There is another explanation for the increasing CO emissions that the oil-rich areas may be formed when the combustion begins to deteriorate, so that CO emissions increase gradually.

More also, Figure 6 exhibits the results of NOx under different BMEP at 1600 and 2200 rpm respectively and it is clear that NOx emissions increased with the enhanced load regardless of what kind of fuel burning, but it did not change noticeably among them. Due to more adequate oxygen of mixture and the lower temperature in combustion chamber under the small load, NOx emissions of biodiesel and its mixtures appeared to be low-high compared with B0. Although, biodiesel has high cetane number and short ignition delay, which is a trend to reduce NOx emissions, the maximum temperature also increased in the combustion chamber with the increased premixed combustion, which is the major factor to increase the production and emission of NOx. Hence, the NOx emissions of biodiesel are less than the diesel slightly at the speed of 2200 rpm.

Figure 7 exhibits the effect of the palm oil monoester on unburned HC emissions at 1600 and 2200 rpm as also investigated in the experiment. It was found that HC emissions displayed the law of fluctuation when four fuels

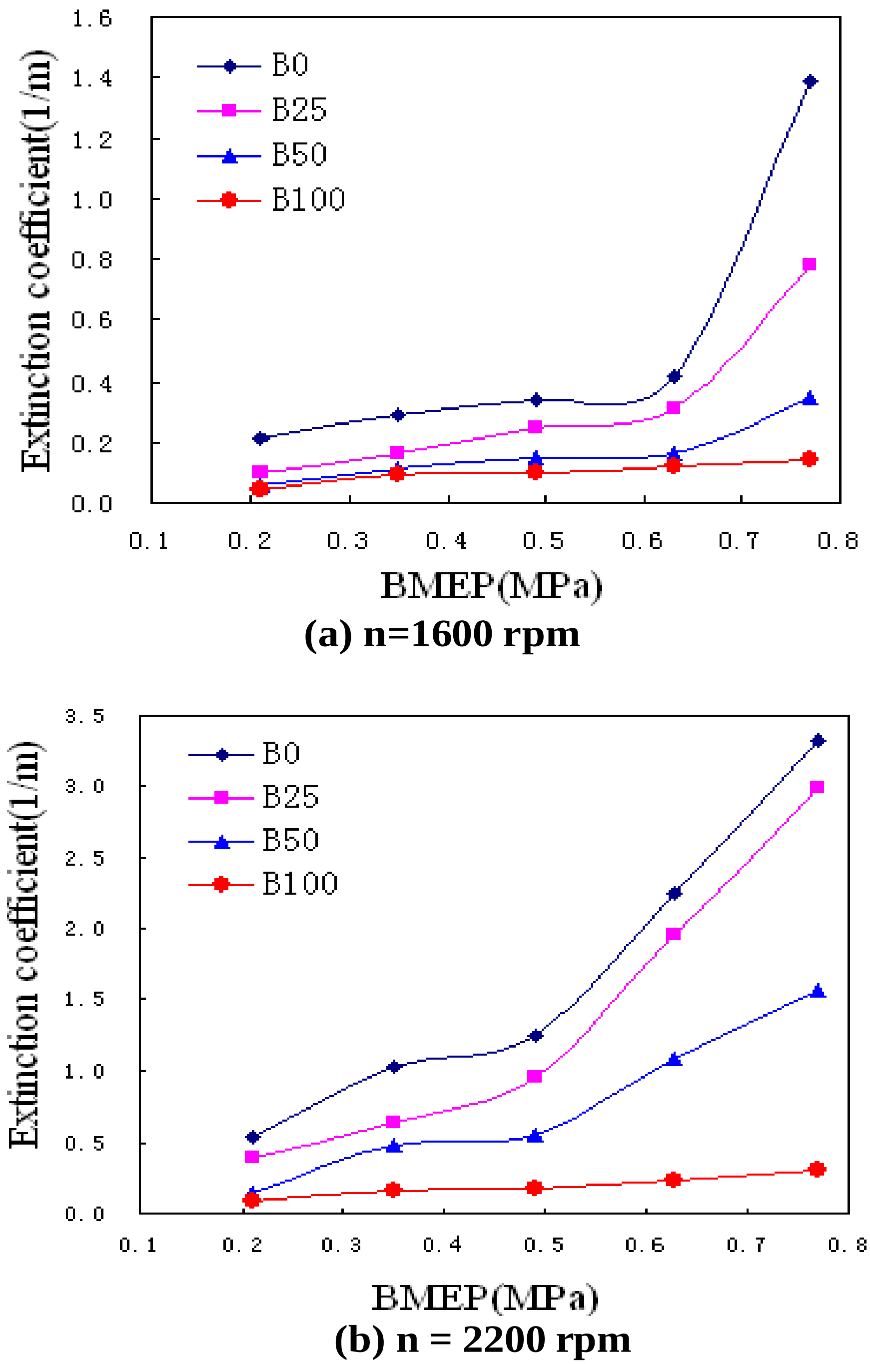


Figure 4. Effect of the palm oil monoester on smoke emissions.

were burnt. However, in two load conditions, HC emissions increased with the oxygen content of fuel. The likely reason was attributed to the lower heating value of biodiesel. When biodiesel is mixed with diesel, the decreased ignition delay of mixture results in the reduction of heat in combustion process, so the temperature of gas starts to drop more suddenly, which makes the quenching layer thickening in chamber. Because fuel in quenching layer is difficult to vapor, there is increasingly unburned HC not participating in combustion as the quenching layer is thickened. When unburned HC is more than the decreased part of HC due to the extra oxygen from oxygenated fuels, HC emissions begin to increase.

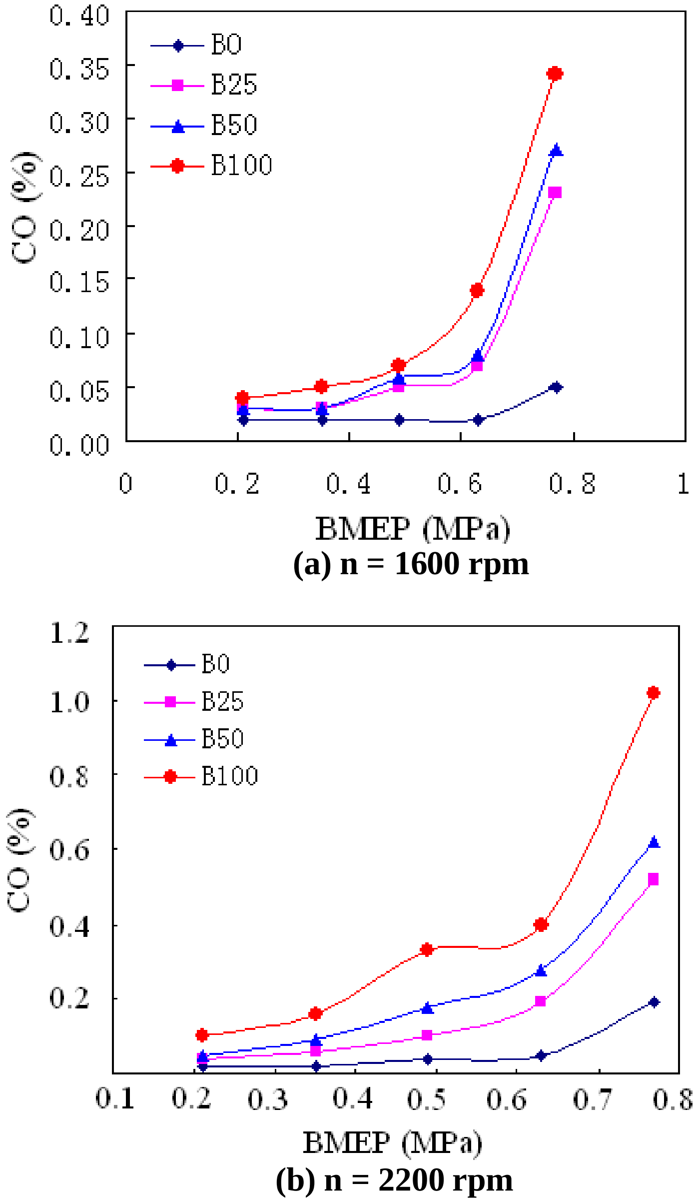


Figure 5. Effect of the palm oil monoester on CO emissions.

Combustion performances

Figure 8 displays the test results of in-cylinder pressure when the tested diesel engine burnt B0, B25, B50, and B100 at 1600 rpm (0.49 MPa) and 2200 rpm (0.63 MPa). Pressure was not noticeably enhanced from the pressure biodiesel with the high oxygen content having more premixed combustion than diesel, which meant that the heat released was so concentrated that the maximum cylinder pressure rises. The in-cylinder peak pressure was raised about 0.3 MPa when burning B100 compared to B0 at 1600 r/min. Similar to the maximum explosion pressure at 2200 r/min, it was also clearly seen that the pressure was increased by 0.2 MPa when B100 is burnt in the place of B0.

Moreover, Figure 9 exhibits the change rates of engine in-cylinder pressure with the crank angle at 1600 and 2200 rpm respectively. From the two figures, it can be easily observed that in-cylinder pressure change rate was close under the engine running modes 1600 rpm, BMEP of 0.49 MPa and 2200 rpm, BMEP of 0.63 MPa when the diesel engine combusted four diesels. The two figures

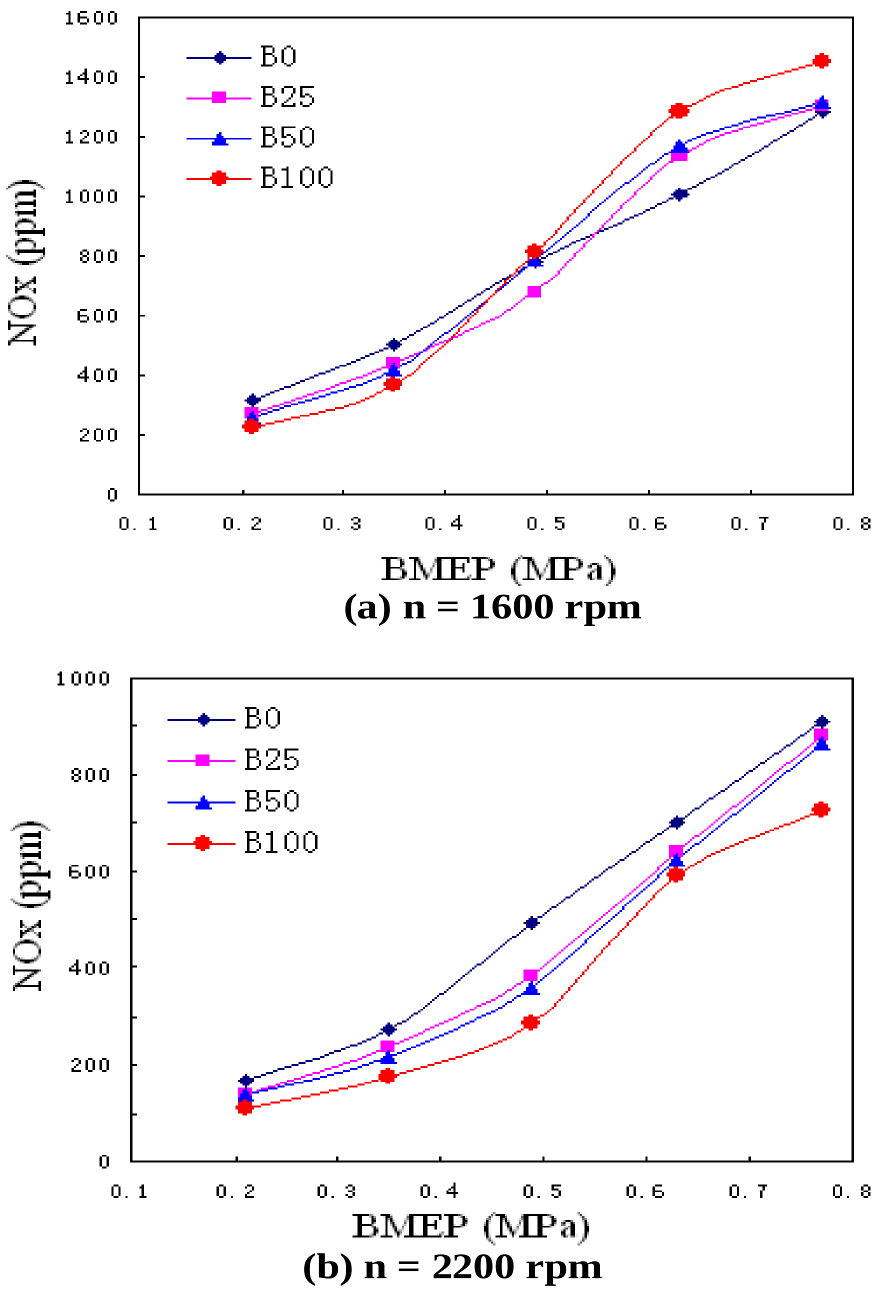
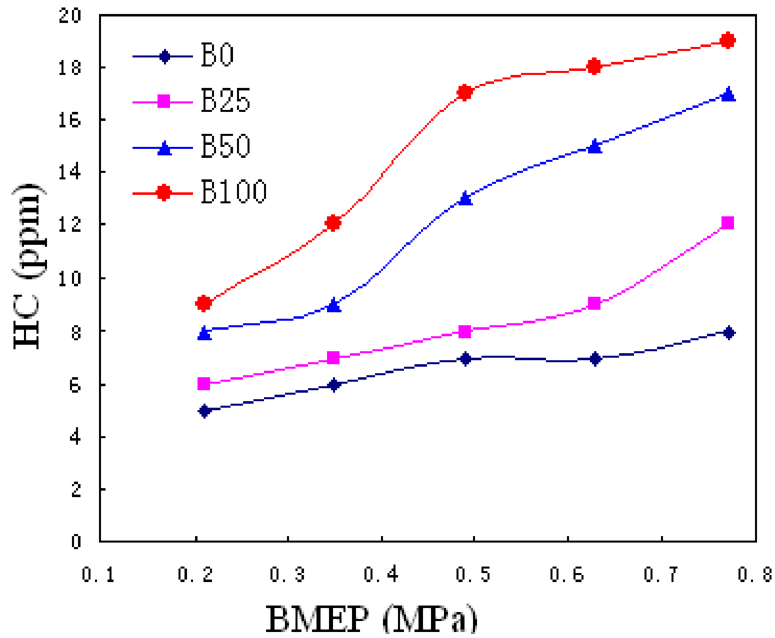


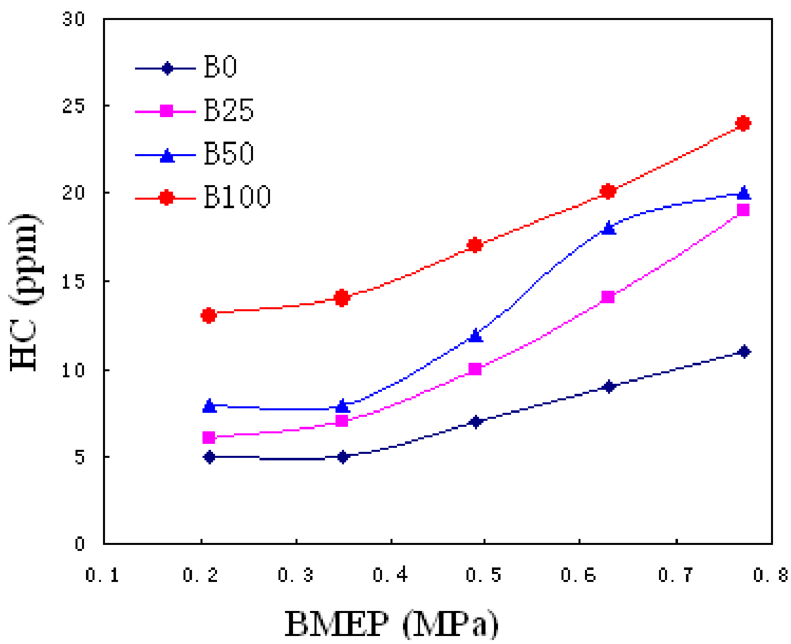
Figure 6. Effect of the palm oil monoester on NOx emissions.

also distinctly revealed that the ignition point of the new biodiesel and its mixture became shorter than that of diesel fuel. This meant that the new biodiesel indeed began to burn earlier than diesel fuel. Also, since the ignition point is mainly affected by the nature of the temperature and fuel, biodiesel's cetane number is higher than diesel with CN45 to 50 currently in China, so it owns good fire performance. Coupled with the temperature increased under high load, the vaporization of biodiesel was accelerated, so that premixed combustion also increased to make the ignition advance. The two aspects decided that ignition delay of biodiesel is less than the ordinary diesel in the conditions of high load.

Furthermore, Figure 10 demonstrates the heat release rates of the diesel engine when it was fueled with the biodiesel, diesel fuel and their mixture. The heat release rate increased when the biodiesel replaced the reference diesel fuel during the experiment under two modes. Only at the mode 1600 rpm and BMEP of 0.49 MPa, was no change observed in the heat release rate. This indicated



(a) n = 1600 rpm



(b) n = 2200 rpm

Figure 7. Effect of the palm oil monoester on HC emissions.

that the combustion velocity of the new palm oil monoester in diesel engine combustion chamber is much higher than diesel fuel as aforementioned. The reason is supposed to be that the oxygen contained in the new biodiesel is able to accelerate the engine combustion. The curves in the two figures also clearly showed that the new biodiesel indeed began to burn earlier than diesel fuel as earlier mentioned. This implies that the cetane

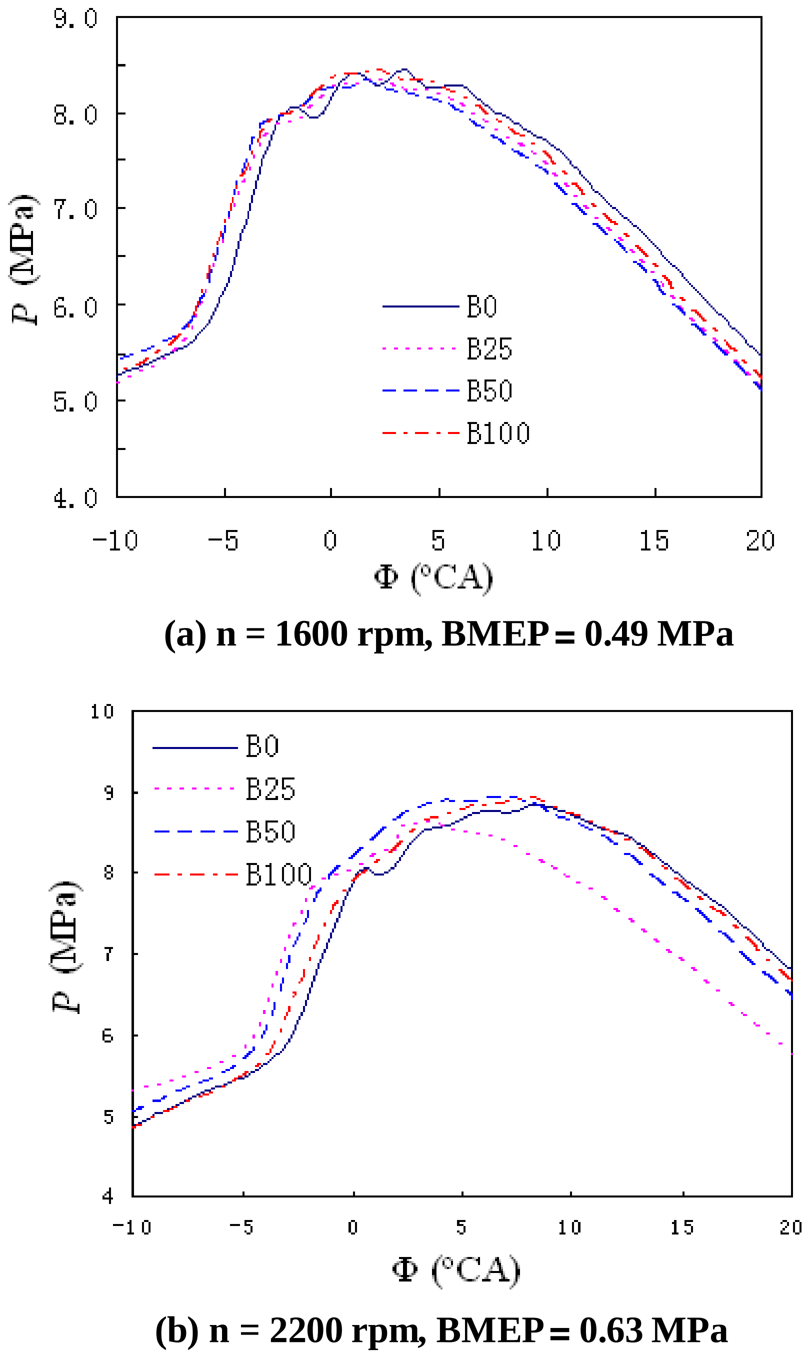
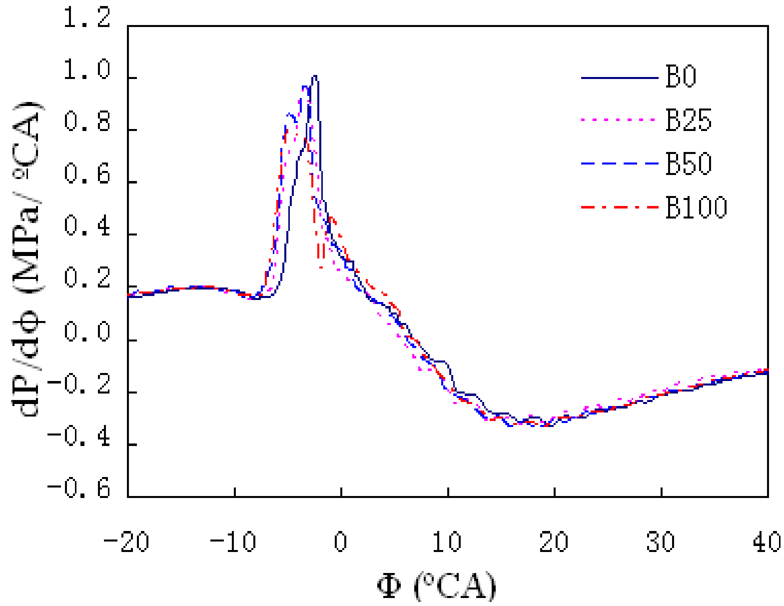


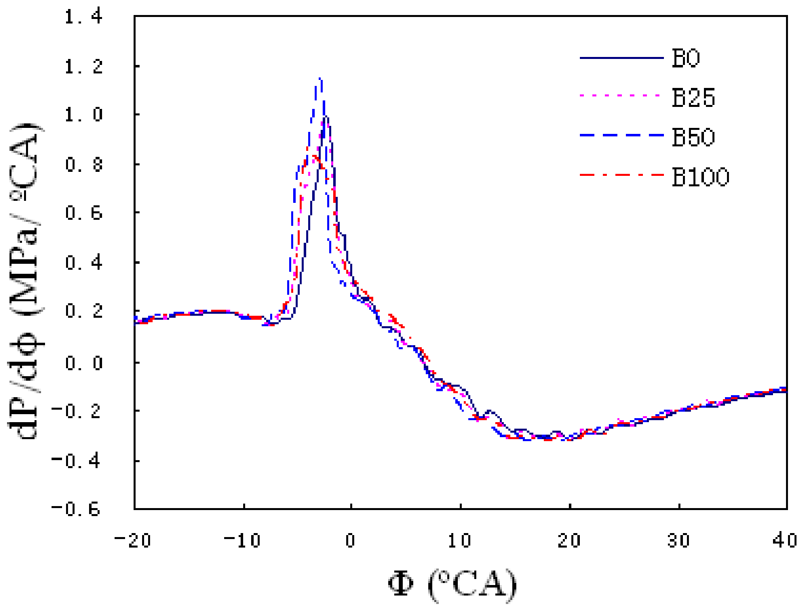
Figure 8. Diesel engine in-cylinder pressure when burning different fuels.

number of the new biodiesel is higher than that of diesel fuel. The reason why the new biodiesel has higher cetane number must be that the ether group introduced was more easily oxidized and released more heat at a given time to raise the temperature to accelerate fuel oxidation. The cetane number of the new biodiesel is being further determined in the laboratory.

Finally, Figure 11 demonstrates the decreased engine thermal efficiency when the biodiesel and its blend with diesel fuel, respectively replaced the reference diesel fuel in the experiment. Result indicates that it decreased as the oxygen content of biodiesel fuel increases. A significant decrease by 0.62~1.11%, 3.28~5.82% and 3.83~8.91% in engine thermal efficiency was also



(a) n = 1600 rpm, BMEP = 0.49 MPa



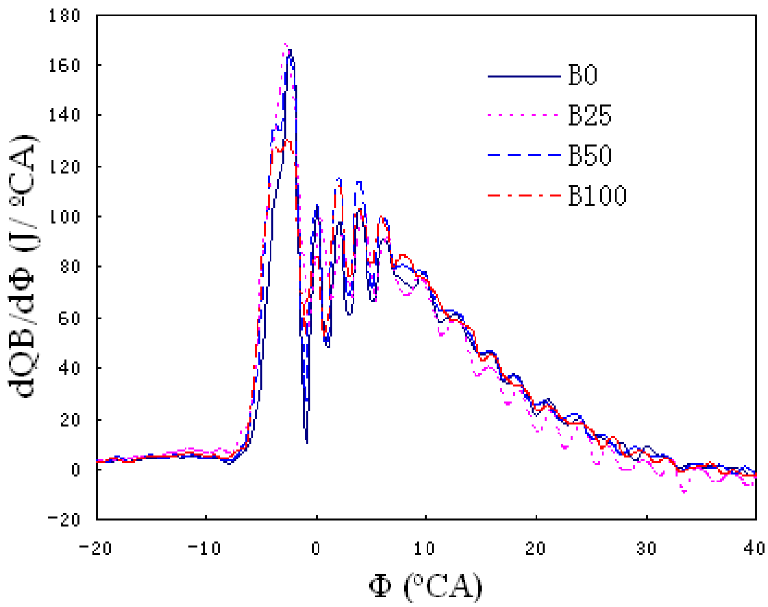
(b) n = 2200 rpm, BMEP = 0.63 MPa

Figure 9. Diesel engine in-cylinder pressure changing rate when burning different fuels.

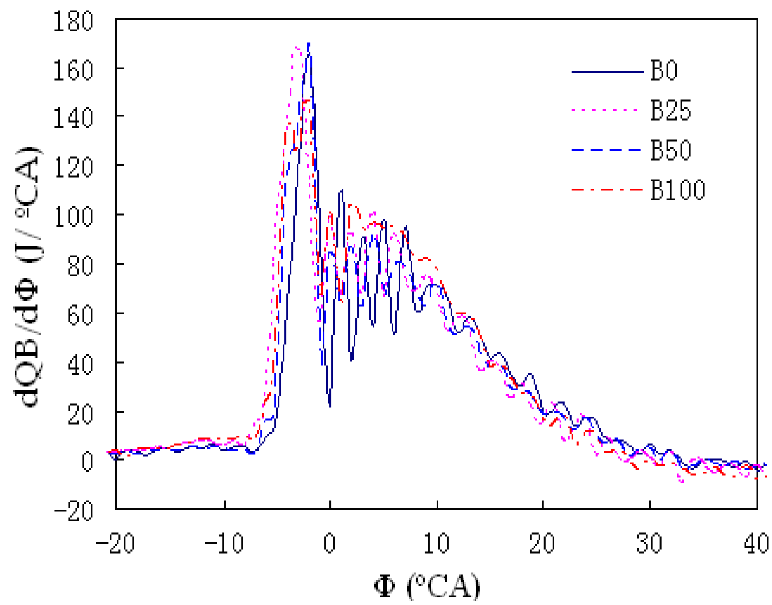
observed when the tested engine burnt B25, B50 and B100 in place of B0 at 1600 rpm. The similar result of 1.47~6.19%, 4.85~10.84% and 5.64~14.4% was also attained at 2200 rpm. The reason is that the new biodiesel contains a certain amount of oxygen which can promote the more complete combustion of the biodiesel than diesel fuel. This may be due to the lower heat value of biodiesel, which causes local hypoxia in the combustion process.

Conclusion

A novel biodiesel named ethylene glycol monomethyl



(a) n = 1600 rpm, BMEP = 0.49 MPa



(b) n = 2200 rpm, BMEP = 0.63 MPa

Figure 10. Diesel engine heat release rate when burning different fuels.

ether palm oil monoester, containing moreoxygen than traditional biodiesel has been prepared and structurally identified by three different technologies. When diesel engine was fueled with this palm oil monoester and its mixture with diesel fuel in the proportion of 1:1 or 1:3 by volume, due to certain amount of oxygen contained in them, engine-out exhaust emissions such as smoke, NOx was substantially reduced under partial load modes, but CO, HC emissions did not change significantly in general, but were rather raised under certain load.

The combustion of the new palm oil monoester can lead to a little higher heat release rate than diesel fuel, and both engine in-cylinder pressure and its changing rate with crankshaft angle increase to some extent

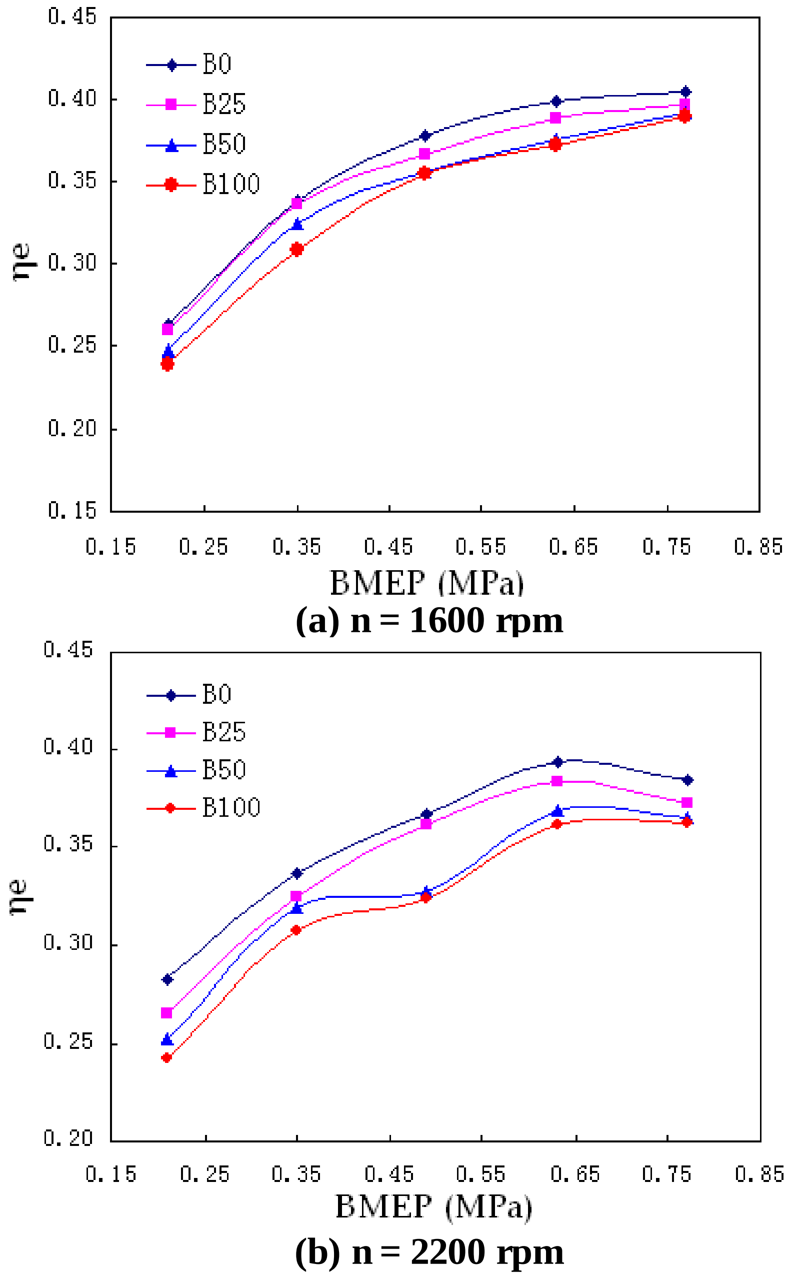


Figure 11. Engine brake thermal efficiency when burning different fuels.

because of its higher cetane number and shorter ignition delay than diesel fuel. Utilization of the new biodiesel can remarkably improve engine brake thermal efficiency, since palm oil monoester is ignited earlier during diesel engine operation.

ACKNOWLEDGEMENT

This research was supported by the National Natural Science Foundation of China (Grant no. 50976125).

REFERENCES

Crooles R (2006). New Findings on Combustion Behavior of Oxygenated Synthetic Diesel Fuels. Biomass Bioenergy, 30(4): 461-468.

Cetinkaya M, Karaosmanoglu F (2007). The Effect of Oxygenated Fuels on Emissions from a Modern Heavy-Duty Diesel Engine. Energy Fuels, 19(8): 645-652.

Davies G, Henrissat B (1995). Structures and mechanisms of glycosyl hydrolases. Structure, 3(8):853-859.

Kaplan G, Arslan R, Surmen A (2006). Modeling the Effects of Oxygenated Fuels and Split Injections on DI Diesel Engine Performance and Emission. Energy Sources, 28(10): 751-755.

Lapuerta M, Armas O, Ballesteros R (2005). Oxygenated Fuels for Particulate Emissions Reduction in Heavy Duty DI Diesel Engines with Common Rail Fuel Injection. Fernandez Fuel, 84(2):773-780.

Pugazhvadivu M, Jeyachandran K (2005). Experimental Studies of the Impact of CETANERTM on Diesel Combustion and Emission. Renewable Energy, 30(12): 2189-2202.

Usta N, Ozturk E, Conkur E (2005). Emission Characteristics of a Navistar 7.3 L Turbo diesel Fueled with Blends of Oxygenates and Diesel. Energy Conversion Manage. 46(6):741-755.

Yuan T, Yang P, Wang Y, Meng K, Luo H, Zhang W, Wu N, Fan Y, Yao B (2008). Heterologous expression of a gene encoding a thermostable beta-galactosidase from Alicyclobacillus acidocaldarius. Biotechnol Lett. 30(2): 343-348.