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Study on exhaust performances and preparation of a new curcas oil biodiesel

First A.Jiang Dayong

Research Institute of Communication, the Engineering University of CAPF, Xi'an, (P.R.CHINA)

E-mail: wanghe717@163.com

ABSTRACT

In order to further enhance the reduction rate in engine-out smoke emissions, now a novel biodiesel named Ethylene Glycol Methyl Ether Curcas Oil Monoester has been developed in the laboratory. The fuel was synthesized with curcas oil and ethylene glycol methyl ether, and the structure was identified through FT-IR and ^{1}H NMR. Because this fuel has one more ester group than the traditional biodiesel, its oxygen content was higher. Engine test results showed that engine-out smoke emissions were decreased by 73.0%–92.9%, and NO_x, CO were also lessened significantly. But unburned HC emissions generally had no noticeable change as compared to pure diesel fuel or mixture of the biodiesel and 0# diesel fuel. Physicochemical test also confirmed that the new biodiesel could be used as a substitute or additive for 0# diesel. With the increasingly stringent for vehicle exhaust pollution control in China, Ethylene Glycol Methyl Ether Curcas Oil Monoester biodiesel should have exciting application prospects.

KEYWORDS

Curcas oil biodiesel;
Preparation;
Characterization;
Physicochemical properties.

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[1-3]. One of the most promising alternative energy sources is biodiesel because it is renewable and available worldwide. A Traditional biodiesel used to be the methyl ester of vegetable oil, which is prepared through transesterification 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[4-6]. However, since there is only one ester group, i.e. two oxygen atoms, existing in each monoester molecule, the oxygen content in such biodiesel is at a comparatively lower level, so the reduction in exhaust 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, and ether groups have excellent fire performance which can improve the ignition performance of the ester group, ie, cetane number. Then the improvement of cetane number can reduce smoke emissions further. In order to enhance the effect of traditional biodiesel in reducing engine-out smoke formation, the introduction of other ether group into its molecule was attempted. Therefore, a novel biodiesel, Ethylene Glycol Methyl Ether Curcas Oil Monoester has been synthesized with commercial refined curcas oil and ethylene glycol methyl ether as reactants in this paper, which has one more ether group than the traditional curcas Monoester. It can be expected to improve performance of engine-out emissions, while improving the fire performance.

As is well known, curcas oil comes from manioca which is one of the forestry plants with the highest rates of oil productivity. Because of its widely adapting to different regions, low-cost planting, and with no need for arable land, there has been large scale cultivation in China such as Sichuan, Guizhou, Yunnan, Fujian and other provinces in recent years. Another raw material, Ethylene Glycol methyl Ether was used for press industry extensively as a common chemical material, whose source and price can be both guaranteed in civil. So the new biodiesel has a greater application value.

EXPERIMENTAL SECTION

Preparation

Initially, the selected curcas oil was treated through extraction with ethanol as solvent at a temperature of 90ºC to remove tiny amount of organic fatty acid about 0.38mgKOH/g in it and then was purified under vacuum condition. FT-IR analysis justified that there was no vibration(–OH) absorption peak in the region of 3200cm^{-1}–3600cm^{-1}, indicating that there was little fatty acid and ethanol in the treated curcas oil in Figure 1.

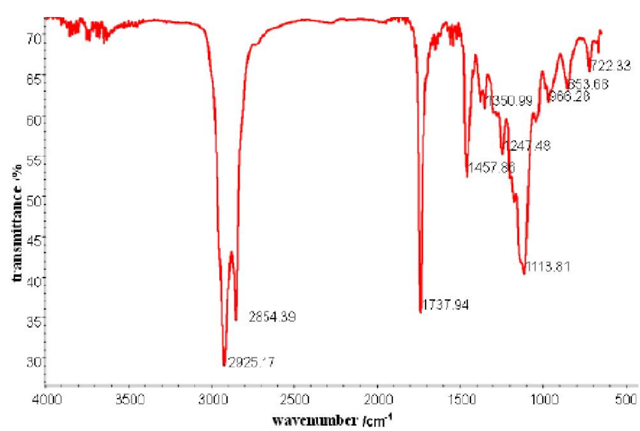

Figure 1 : FT-IR spectrogram of curcas oil after treatment

The subsequent transesterification reaction was carried out in a flask with the acid-free curcas oil of 300ml and ethylene glycol methyl ether of 110ml at a temperature of 60ºC using 1.2% KOH as catalyst, speciûcations of some used chemicals in preparation were present in TABLE 1. Upon completion of the reaction which lasted for approximately 0.5h, the crude product was firstly neutralized with diluted HCl solution and separated from the water phase. Subsequently, it was purified in a vacuum to remove ethylene glycol methyl ether left over in the ester phase after 12h. Finally, it was dried using $CaCl_2$ agent, and the yield of biodiesel in laboratory can be close to 90%.

Structure analysis

The chemical structure analysis was conducted with FT-IR and P^{1P}H NMR analytical techniques[7,8]. The test conditions were also confirmed.

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.

Physicochemical properties

As additives or substitutes of 0# diesel, the new biodiesel should meet the use standards for diesel engine. Selecting the different volume ratio of biodiesel with 0-100% respectively, some important physicochemical properties were test at temperature of 25ºC, including miscibility, smoke point, kinematic viscosity, solid point, closed cup flash point and so on.

Engine test

A single cylinder, four-stroke, water-cooled, DI diesel engine was adapted to complete determination of exhaust emissions 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 CS20000 Data Gathering & Analyz-

TABLE 1 : Specification of the used chemicals in experiment

Chemicals	Density(g/cm^3)/20°C	Boiling point (°C)	Molecular weight	Standard
curcas oil	0.917	—	857.0	Primes state
ethylene glycol methyl ether	0.913	134	76.1	analytically pure
ethanol absolute	0.789—0.791	78	46.1	analytically pure
potassa	950	—	23.5	chemically pure

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

ing System was utilized to process data.

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 curcas 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 performances.

The engine tests were carried out under the following condition: ambient temperature of 23°C, humidity of 86%, and engine water-cooling temperature of 95°C. In the experiment, when the engine went into 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 listed the main absorption frequencies displayed in IR spectrum obtained for the new curcas oil monoester. No absorption peaks above 3100cm-1 was found, implying that there is no hydroxyl group (-OH) in the synthesized product. Therefore, it was easily confirmed that the product is an ester involving ether group.

Figure 3 and TABLE 4 illustrated P1PH NMR data gained for the curcas oil monoester. Chemical shift 5.342 ppm belongs to the protons attached to C=C group in the molecules, while chemical shift 4.227 ppm, 3.593 ppm, 3.393 ppm respectively belong to the protons existing in the group -COOCH2CH2OCH3 in the order from the left to the right. More peaks occurring in the chemical shift region below 3.000 ppm all are attributed to protons in the fatty groups (-R) and other

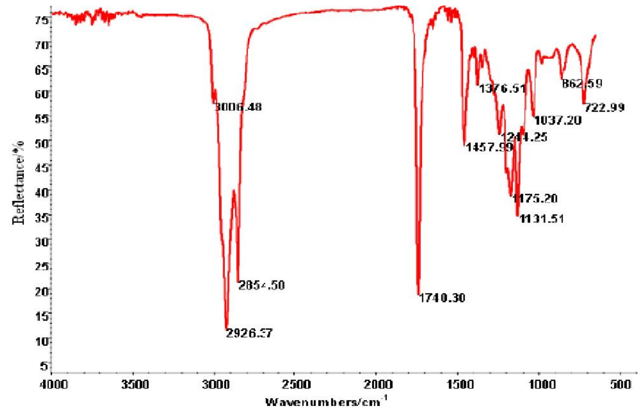

Figure 2 : FT-IR spectrum of curcas oil monoester

TABLE 3 : FT-IR spectrum data of Curcas Oil Monoester

Frequency (cm^{-1})	Group attribution	Vibration type	Strength
2926.37	-CHB$_{3B}$, -CHB$_{2B}$	νB$_{asB}$	s
2854.50	-CHB$_{3B}$, -CHB$_{2B}$	νB$_{sB}$	s
1740.30	C=O	ν	s
1457.99	-CHB$_{2B}$	δ	m
1244.25	-CHB$_{3B}$	δ	m
1175.20	C-O-C	νB$_{asB}$	m
1131.51	C-O-C	νB$_{sB}$	m
722.99	$(CH_2)_n$ (n>4)	-	w

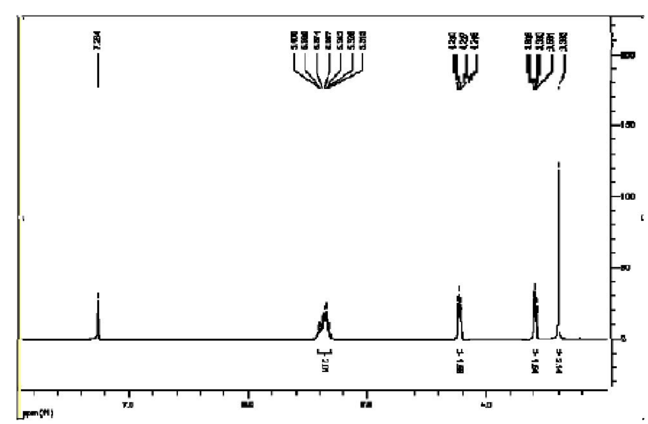

Figure 3 : ^{1}H NMR wave spectrogram of Curcas Oil Monoester

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 4 : P1PH NMR Data of Curcas Oil Monoester

chemical shift(ppm)	proton peak splitting	coupling constant(Hz)	*peak area/* proton number
5.342	triplet	6.4	1.281/-
4.227	triplet	3.6	1.56/2
3.593	triplet	3.6	1.54/2
3.393	singlet	—	2.14/3
<3.000	more	—	more

Physicochemical properties

Solution experiment showed that Ethylene Glycol Methyl Ether Curcas Oil Monoester can be mixed miscible with 0# diesel in terms of any proportion and temperature. Figure 4 also exhibited that other physicochemical properties have good performance so that it can be used as additives of diesel fuel or substitutes alone.

Exhaust emissions

Two types of engine operation modes running at 1400 rpm and 2000 rpm were respectively selected to study the changes of exhaust emissions under different partial brake mean effective pressures (BMEP).

Figure 5 displayed the effects of the new curcas oil monoester on engine-out smoke emissions at 1400 rpm and 2000 rpm respectively, and it was very clear that a considerable decrease had been approached. When the engine burnt the B25 under partial loads at 1400 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 2000 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 were known 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 mainly generated in the diffusion com-

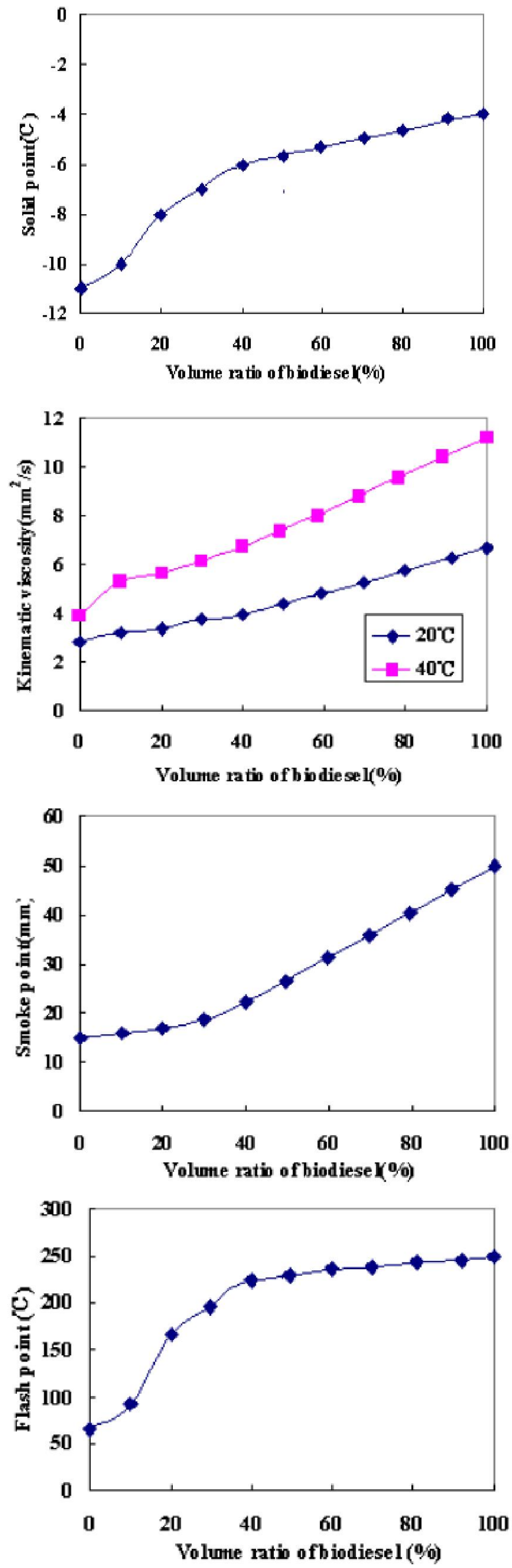

Figure 4 : Effect of Curcas Oil Monoester on phypsychochemical properties

bustion, oxygen capacity can be improved 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.

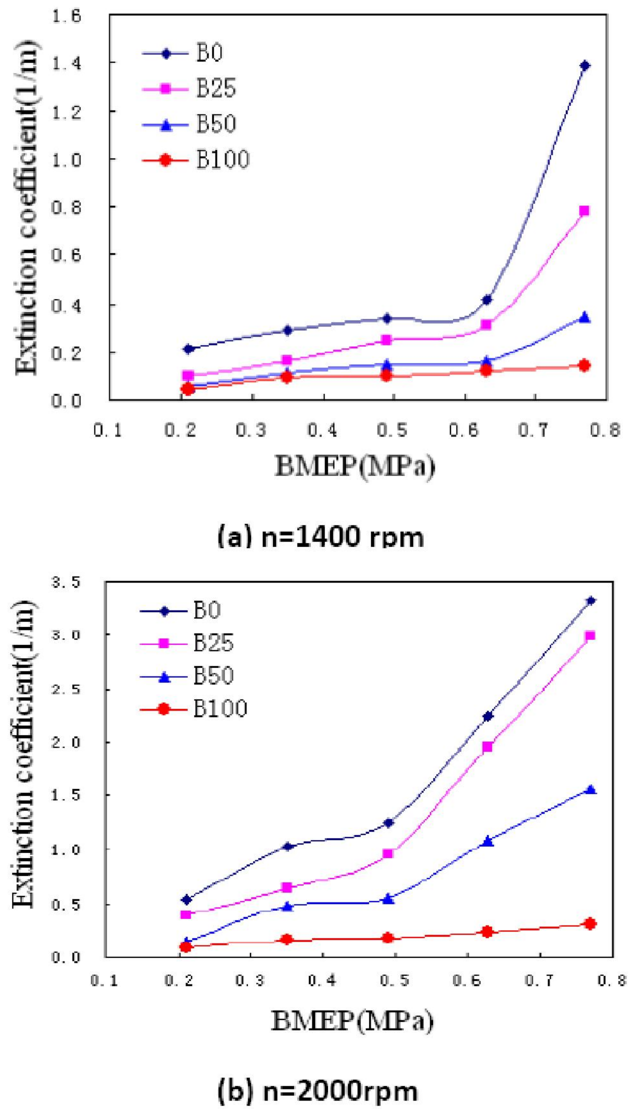

Figure 5 : Effect of Curcas Oil Monoester on smoke emissions

Figure 6 presented the test results of CO emissions under different BMEP at the speed of 1400rpm and 2000rpm. The figures reveal that at the low load CO emission does not change significantly, and with increasing of loads, CO emissions also increase rapidly. When the BMEP is low, the engine is 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 is 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.

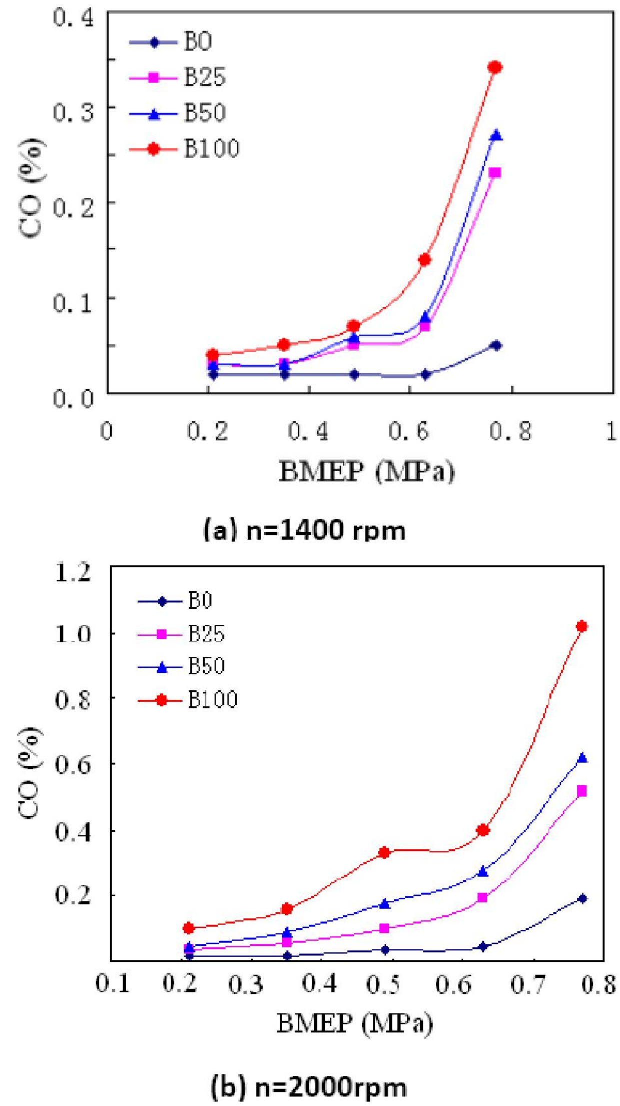

Figure 6 : Effect of Curcas Oil Monoester on CO emissions

Figure 7 exhibited the results of NOx under different BMEP at 1400 rpm and 2000 rpm respectively, and it is clear that NOx emissions increase with the enhancing load regardless of what kind of fuel burning, but it did not change noticeably among all tested fuels. 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 appears 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, but 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. So the NOx emissions of biodiesel are less than the diesel slightly at the speed of 2000rpm.

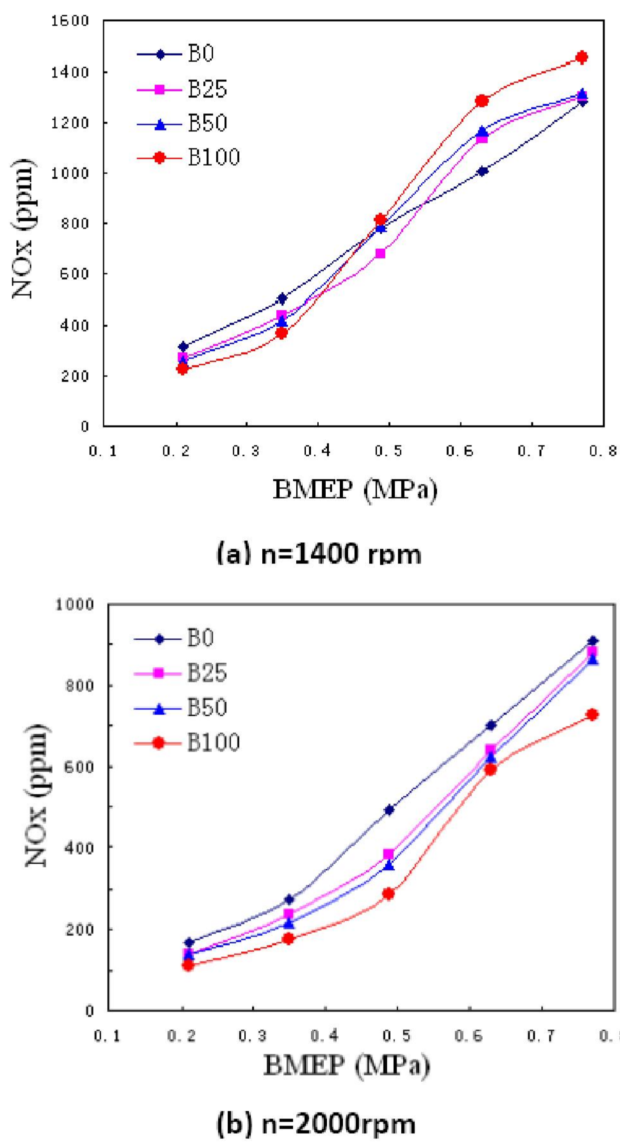

Figure 7 : Effect of Curcas Oil Monoester on NOx emissions

Figure 8 exhibited the effect of the curcas oil monoester on unburned HC emissions at 1400 rpm and 2000 rpm were also investigated in the experiment. It was found that HC emissions display the law of fluctuation when four fuels were burnt. But in two load conditions, HC emissions increased with the oxygen content of fuel. The likely reason is 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 more and more 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.

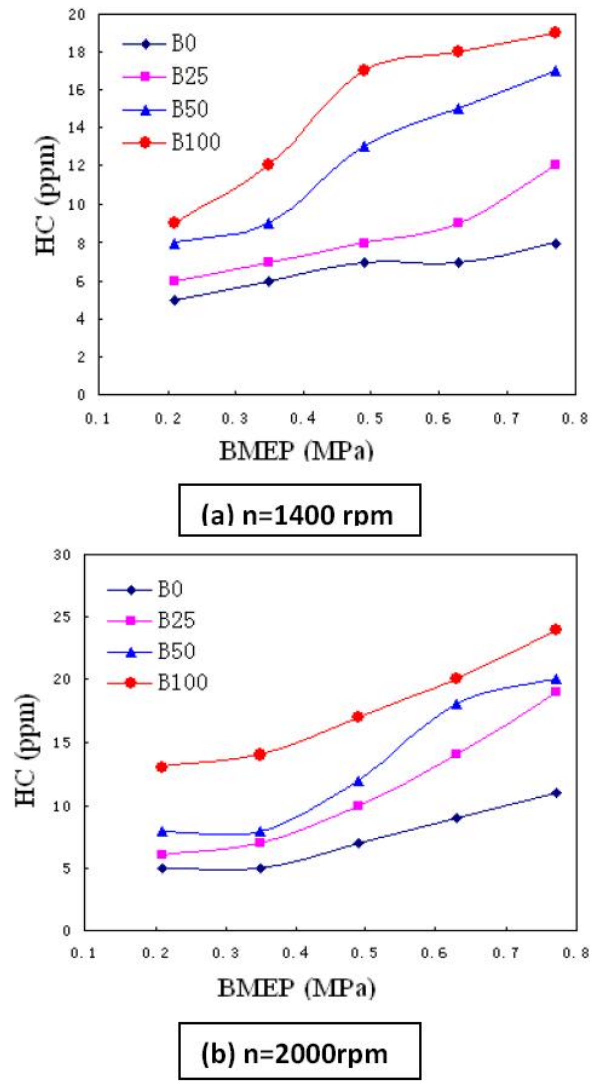

Figure 8 : Effect of Curcas Oil Monoester on HC emissions

CONCLUSIONS

A novel biodiesel named Ethylene Glycol methyl Ether Curcas Oil Monoester containing a higher amount of oxygen than traditional biodiesel has been prepared.. Some important physical chemical properties of the new curcas oil monoester are proven to have good performance in terms of any proportion with 0# diesel and temperature.

When diesel engine is fueled with this curcas oil monoester and its mixture with diesel fuel in the proportion of 1:1 or 1:3 by volume,, engine-out exhaust emissions such as smoke, NOx can be substantially reduced under partial load modes, but CO, HC emissions have no significant change, even when risingcertain load.

This fuel has good characters in economy and engine out emissions, which can be used as additives or substitutes for 0# diesel.

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