

Review

A Review of the Developed New Model Biodiesels and Their Effects on Engine Combustion and Emissions

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Abstract: Biodiesel is regarded to be a renewable, CO₂ neutral and thus sustainable biological alternative diesel fuel. With attention to the reduction of petroleum import, PM 2.5 aerosol particles and the greenhouse effect gas CO₂, biodiesel has drawn great research interests and efforts in the past decade in China. Generally, biodiesel refers to fatty acid methyl ether (FAME) which has a proved effect in reducing diesel emission, particularly PM. However, FAME has a limited cetane number and oxygen content, to study the effects of elevated cetane number and oxygen content on fuel properties, engine combustion and emissions, ethylene glycol monomethyl ether is used to produce a series of new models of biodiesels by transesterification method. The feedstocks are rapeseed oil, soybean oil, peanut oil, palm oil and cottonseed oil. Ether group alcohols used in this study include ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, propylene glycol monomethyl ether, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether. The molecular structure was proved by FT-IR and NMR analyses. Fuel properties were measured based on the corresponding standards. The developed new model biodiesels have cetane number (CN) over 70 and oxygen content over 17% by mass, which are higher than FAME (50 CN and 11% oxygen). They have the same level of lower heating value as FAME, but have a higher density, which helps to compensate the decrease of engine power. Meanwhile, the engine tests were carried out to investigate the effects of ether ester group on engine combustion and emissions. The test results show that FAME reduced smoke 30% to 50%, while the new model biodiesel fuels reduced engine smoke as high as 80% and have the potential to decrease engine HC, CO and NO_x emissions 50% or more.

Keywords: biodiesel; ethylene glycol monomethyl ether; engine; combustion; emission

1. Introduction

Diesel engines are robust, powerful and efficient enough, therefore they are widely used in trucks, off-road vehicles, farming machineries, electricity generation plants and so on. More and more diesel engines are put into use which consumed a great quantity of diesel fuel. For example, as showed in Figure 1, in 2017 in China, about 180 million tons of diesel fuel had been consumed [1]. As it is known, diesel engine heterogeneous combustion occurred within its cylinders results in higher NO_x and PM emissions [2,3]. The statistic data of the regulated pollutants of CO, HC, NO_x and PM of vehicles are showed in Figure 2, which is cited from China Vehicle Environmental Management Annual Report (2018) [4]. It can be seen that diesel vehicles contribute almost 100% PM and 68.3% NO_x emissions of

vehicles. To give a direct impression about the share rate, for example in Beijing, the vehicles contribute about 45% of total air PM 2.5 pollution.

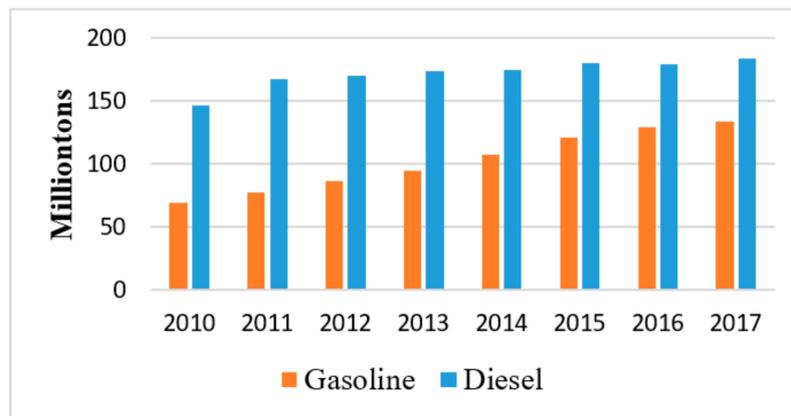


Figure 1. The statistic gasoline and diesel consumption from 2010 to 2017 [1].

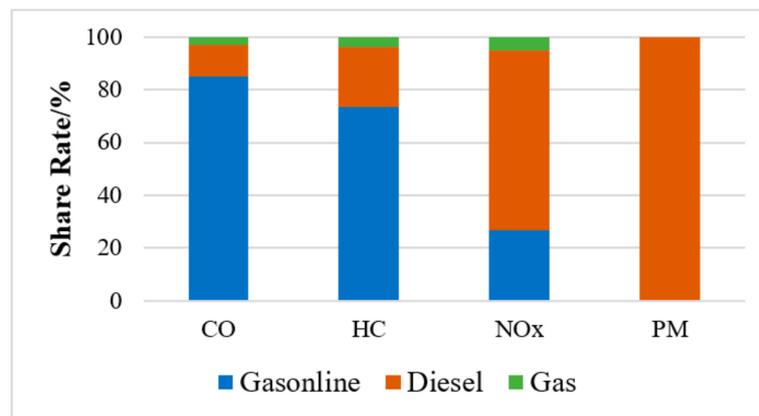


Figure 2. Vehicle emission share rate according to fuels [4].

Biodiesel was thought to be CO₂ neutral and sustainable. With attention to the reduction of PM 2.5 and the greenhouse effect gas CO₂, it drew great research interests and efforts in the past decade and got a rising market world widely. Therefore, China is so confident to carry out biodiesel application programs to control the emission from diesel vehicles following the world trend and to cease the pressure of petroleum importation as well.

The biodiesel market entered a booming period since 2006 and reached a key milestone in 2011 to follow the United Nations Framework Convention on Climate Change in the world, which is showed in Figure 3. Figure 3 also shows a similar development trend of biodiesel in the US, EU and China [5–7]. In the US, 2016 market was a record high of 2.8 billion gallons according to EPA figures showed in Figure 4. In Europe Union, driven by the Renewable Energy Directive, biodiesel should be 10% till 2020. The produced and imported quantity of biodiesel in 2017 was 14 million tons according to Figure 5. It was about 10% of biodiesel in transport diesel approximately. In China, promoted by China the 12th and 13th Five-Year Plan for Renewable Energy Development [8,9]. Biodiesel Industry Development Policy [10], it can be seen from Figure 6 that the development of the domestic biodiesel market has truly entered a booming period after 2013. In 2017, China biodiesel production is about 1.1 million tons. Even if 5% biodiesel is added to the petrodiesel, the market will be at least 9 million tons accordingly. There is a vast market space for the development of biodiesel. So, it is important to carry out studies of biodiesel for its application in engines, especially in China.

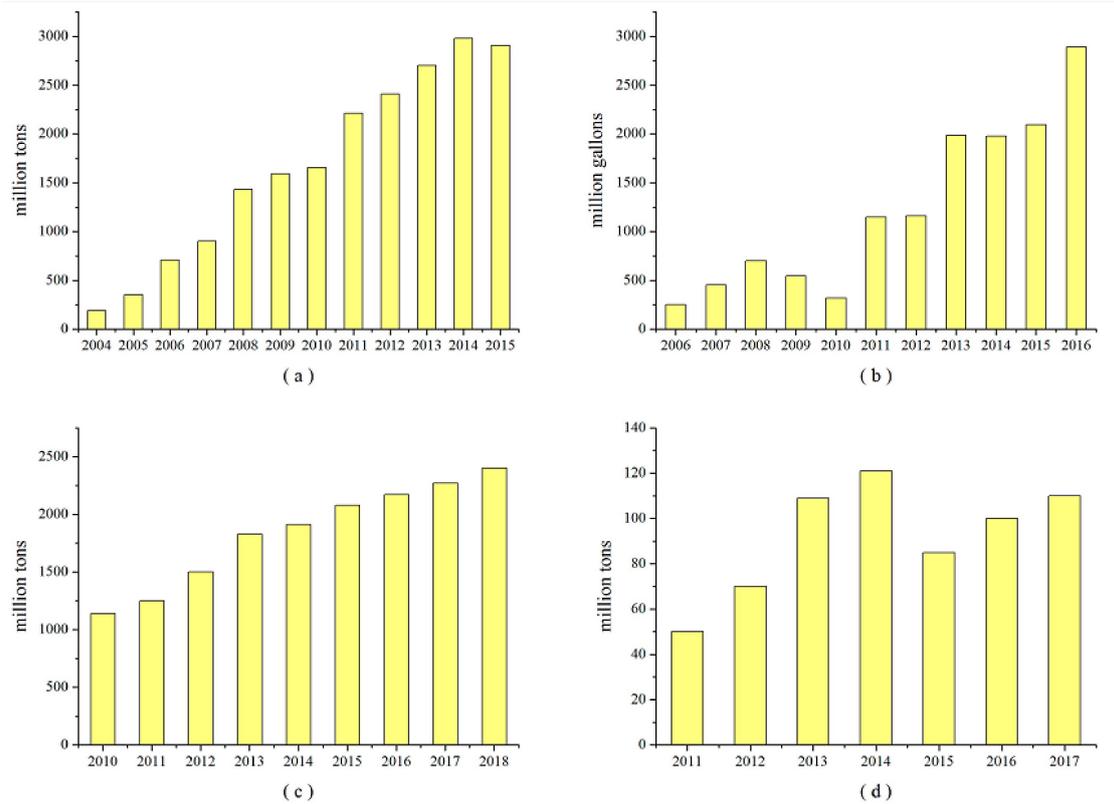


Figure 3. (a) Worldwide biodiesel productions; (b) US biodiesel market; (c) Biodiesel consumption in EU; (d) China biodiesel production from 2013 to 2017 [5–7].

A number of studies have examined the emission impacts of biodiesel [5,11–17]. The commonly accepted results are showed in Figure 4 from a US DOE report [18]. It can be seen that more biodiesel means better reduction of CO, HC and PM of the engine, however, biodiesel was mostly used with petrodiesel in a lower proportion due to the fuel properties of density, viscosity, oxidation stability, et al., and their complex effects on the fuel spray atomization, evaporation and combustion. In practice, most countries allow 5% or less than 10% blending with petrodiesel. For example in the quality of European diesel fuels, it is specified by the EN 590 standard, FAME content is 7% as regulated by Directive 2009/30/EC [19].

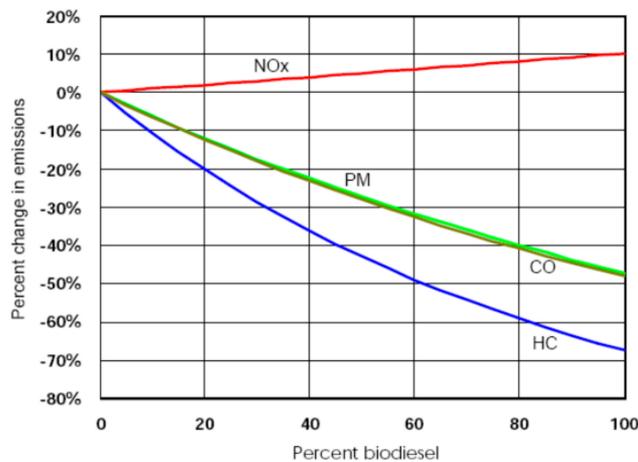


Figure 4. Trends in percentage change of pollutant emissions with biodiesel content [18].

There are several advantages and disadvantages for the application of biodiesel as engine fuel [5,11–17,20]. They are summarized as below.

1. It is renewable, safe and biodegradable. Biodiesel can be made from vegetable oils, animal fats, or recycled restaurant greases (waste cooking oils). Both the original materials and the product of biodiesel are safe and can be degraded naturally.
2. It can reduce greenhouse gas emissions. A life cycle analysis of biodiesel showed that overall CO₂ emissions were reduced by 78% compared with petrodiesel fuel, which will contribute to domestic and international targets of greenhouse gas reductions.
3. It has a similar cetane number as compared to petrodiesel, so it can be used alone, or blended with petrodiesel in any proportions.
4. It is an oxygenated fuel without sulfur content, which can promote engine combustion and reduce emissions of HC, CO and PM, which helps to reduce the environmental pollution.
5. It has better lubricity, and unsaturated esters possess a slight advantage. So, there is no need to reconsider the lubricity of the engine fuel injection system when biodiesel is applied.
6. It is a mix of mono-alkyl esters of long chain fatty acids. It has a higher cloud and pour point (CP and PP) temperatures, density, and kinematic viscosity as well as the acid value compared to diesel, affecting the utility of the fuel, especially in cold conditions.
7. The calorific value of biodiesel is about 37.27 MJ/kg. There is 9% lower than regular petrodiesel. Fuel injection systems measure fuel by volume, and thus, engine output power may be affected under high ratio or pure application conditions.
8. It comprises of saturated and unsaturated esters. Saturated fatty esters are very stable, while unsaturated esters are likely to react with oxygen, therefore reduce oxidation stability.
9. And finally, because of its renewable feature, the use of biodiesel can reduce its dependence on foreign fossil fuels. Sustainable energy supply is necessary for the economic development of a country like China, whose petroleum depends much on import.

For the application of biodiesel, cetane number is the most concerned parameter. The CN of most conventional biodiesel are around 50, which meet the requirement of CI engine, especially under low fraction blending application [21–26]. However, the effects of reducing exhaust emissions are not so significant. There were studies showed that the improvement of CN may results in reduction of biodiesel engine emissions. Higher CN leads to lower NO_x, higher oxygen content decreases CO, HC, PM emissions [27–30]. So, instead of methanol, substances containing more oxygen should be adopted to increase CN and oxygen content for biodiesel.

Conventional biodiesel is prepared through transesterification of vegetable oils or fatty oils with methanol. There are only two oxygen atoms existing in biodiesel molecule, hence the oxygen content in conventional biodiesel is not high. Although the conventional biodiesel has high cetane number (about 50) as petrodiesel, it has not evident competition superiority [21–24,26,27,31,32]. The developed new model biodiesel is synthesized through transesterification reaction of vegetable oils and ethylene glycol ether derivatives. The ether group introduced into biodiesel molecule promotes its octane number and oxygen content to 70 and 17% approximately, which finally proves to have a better performance than conventional biodiesel in reducing engine emissions, especially smoke can be reduced 80% approximately.

This review is to summarize our researches about the new model biodiesels. Transesterification processes were simply described and proved to be the same as FAME. The synthesized biodiesel itself, its fuel properties, engine test equipment and engine performance were reviewed respectively, which proves our research activity is interesting and progressive.

2. New Model Biodiesels and Their Fuel Properties

2.1. New Model Biodiesels

For transesterification, the interest was focused on ethylene glycol monomethyl ether. Ethylene glycol can be made by methanol, as well as ethylene glycol monomethyl ether. They are cheap, small

molecular with high oxygen content, high cetane number. In this case, the produced biodiesel may have a reasonable price to compete with petrodiesel.

The new model of biodiesel is synthesized just like FAME, ethylene glycol monomethyl ether first reacts with catalyst, see sodium (Na) in Equation (1). Sodium ethylene glycol monomethyl ether is formed, and then it is mixed with vegetable oils like rapeseed oil, palm oil, et al. Transesterification reaction occurs as described in Equation (2) with an optimized reactants fraction. The chemical process completes under moderate condition like 60 °C, water bath at atmosphere pressure in laboratory. The mixture should be treated by phase separation, hydrochloric acid (HCl) washing, filter, dry, and finally, new model biodiesel is obtained. The procedures can be simply showed in Figure 5.

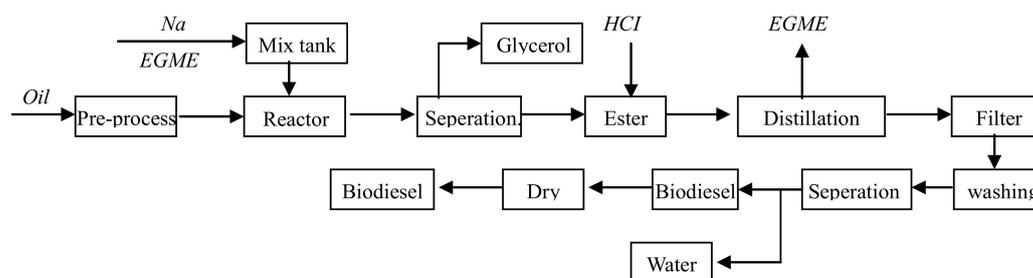
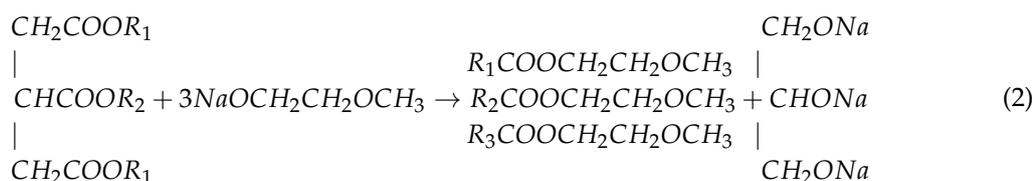


Figure 5. Biodiesel producing processes.

The chemical structure of the synthesized biodiesel can be identified through Fourier transform infrared (FT-IR) spectrum and proton nuclear magnetic resonance (^1H NMR) spectrum analyses [33,34]. Different groups, such as methyl, methylene, carbonyl, C-O-C and C=C, etc., possess distinct vibrational frequency and generate different characteristic infrared absorption spectrum. Furthermore, protons attributed to different group under different chemical environment in the molecule also have quite different characteristic chemical shifts, splitting multiplicity and coupling constants. Based on these obtained characteristic data, the chemical structure of the new model biodiesel can be deduced. In addition, analyses by gel permeation chromatography (GPC) can acquire the data of average molecular weight and molecular weight distribution of the new model biodiesels as well as its originating vegetable oil. The GPC data can be used to make a comparison between the biodiesel and the vegetable oil to further confirm the chemical structure of the new model biodiesel.

2.2. Biodiesel Fuel Properties

Biodiesel is produced by different feedstocks, such as soybean oil in US, rapeseed oil in EU, palm oil in Southeast Asia countries and so on, according to their planting production [22]. China is known to feed one fourth global population by too less farm land, so biodiesel is thought to be made by nonedible oil, waste cooking grease oil. The most developed oils were from *Jatropha curcas*, *Pistacia chinensis*, et al., which can be planted in the mountain areas such as Guizhou and Hainan Provinces [21]. Different stocks have different length, structure and content of mono-alkyls. Some 11 common feedstocks of biodiesel are showed in Table 1. The length of most chain is 16 or 18, some contain 1 or 2 or 3 unsaturated olefinic bonds. The number of olefinic bond and their containing percentage are used to calculate Degree of Unsaturation (DU). The available researches proved that there is a negative correlation between the DU and CN of biodiesel. Biodiesels are used in CI engines,

their CNs are very important parameters. It was correlated in Equation (3). According to their Degree of Unsaturation, their Cetane Number can be estimated [24], and the results are listed in the Table 2, as well.

$$\text{CN} = 65.0958 - 0.1209 \times \text{DU} \quad (3)$$

The oxygen content is generally measured by element analysis method. Available data are given in Table A1 in Appendix A [21–24,26,27,31].

It can be seen that the cetane number and oxygen content of FAME are around 50 and 11%, which are less affected by oil stocks. To improve these fuel properties, new types of biodiesel were developed. Ethylene glycol monomethyl ether was mostly used to react with different vegetable oils to synthesize different biodiesels, so that their effects of ether group and fatty acids on engine combustion and emissions can be compared. Meanwhile ethylene glycol ethyl ether and propyl ether types biodiesels and diethylene glycol and triethylene glycol monomethyl ether types of biodiesels were developed to understand their effects. Table 1 lists some of new types of biodiesels and their fuel properties our group developed in recent years [32–50].

Table 1. New models of biodiesels and some of their fuel properties [32–50].

Oil	Alcohol	Product	Density	LHV	OC	CN
0# diesel	/	0# diesel	860	42.5	0	50
Rapeseed Cottonseed	methanol	RCOOCH ₃	884 886	/ 37.5	10.9 10	51 52
Rapeseed Soybean Peanut Cottonseed	ethylene glycol methyl ether	RCOOCH ₂ CH ₂ OCH ₃	910 907.2 939.1 901.5	38.7 38.5 37.0 38.5	/ / / 14.3	/ 66 / 70.1
Palm Soybean	ethylene glycol ethyl ether	RCOOCH ₂ CH ₂ OC ₂ H ₅	893.4 902.7	36.2 38.6	/ /	80.4 /
Palm	ethylene glycol n-propyl ether	RCOOCH ₂ CH ₂ OC ₃ H ₇	/	37.3	16.35	72.3
Palm	propylene glycol methyl ether	RCOOCH(CH ₃)CH ₂ OCH ₃	889.2	/	/	/
Cottonseed	diethylene glycol methyl ether triethylene glycol methyl ether	RCO(OCH ₂ CH ₂) ₂ OCH ₃ RCO(OCH ₂ CH ₂) ₃ OCH ₃	912.0 935.5	37.0 35.8	16.88 18.90	76.9 80.9
Standard			ASTM	ASTM	ASTM	ASTM

The new types of biodiesels have a CN around 70, oxygen content about 17%, which are higher than FAME.

3. Test Engine and Parameter Measurement

A single cylinder diesel engine was adopted in these studies. It is water cooled and natural aspirated. The main technical specifications are listed in Table 2. A twin cylinder, water cooled and natural aspirated diesel engine with the same emission level was applied, too. Its specifications are listed in Table 2.

Table 2. Single and Twine cylinder diesel engine parameters.

Engine Type	2102 QB	TY1100
Bore × Stroke (mm)	102 × 115	100 × 115
Displacement (cm ³)	1880	903
Chamber shape	ω	ω
Compression ratio	17.5:1	18:1
Rated power (kW) @ speed (r·min ⁻¹)	23.5/2300	11/2300
Injector type	ZCK154S432	ZCK154S432
Nozzle hole number—diameter (mm)	4 × Φ0.3	4 × Φ0.3
Delivery timing (deg. BTDC)	25	25
Injection pressure (MPa)	19.0	19.0

The biodiesel used in the tests were laboratory produced. They ran the test diesel engines purely or mixed with China 0# petrodiesel of that time in several different ratios. Some of the related fuel properties are listed in Table 1. The blended fuel properties can be referred in the related literatures. During the tests, the engine was kept under warmed up condition at water temperature of 80 °C and lubricant oil temperature of 60 °C. The change of fuels followed a standard schedual in case of mixing with the former fuel.

The test conditions were mainly compared at 1400 r·min⁻¹ and 2200 r·min⁻¹, the max torque speed and the related speed conditions, respectively. The applied equipment in the engine tests were Kistler pressure sensors and DL750 Data Acquisition System, AVL DiGas and DiSmoke, et al. Engine combustion and emissions data were focused here and compared with the results of the pure petrodiesel operation. The experimental setup for engine combustion performance and emissions measurement is shown in Figure 6. An electrical eddy-current dynamometer was applied to determine the engine torque and brake mean effective pressure (BMEP) can be calculated. An AVL DiSmoke4000 opacimeter was used to record smoke number expressed in extinction coefficient. A five-gas analyzer of type AVL DiGas4000 light was utilized to examine NO_x, CO and HC emissions on-line. A Kistler pressure sensor, a charge amplifier and the DL750 Data Acquisition System were adopted to measure and record the cylinder pressure, then the heat release rate can be computed according to the First Law of energy conservation and the relationship between crank angle degrees and cylinder volume.

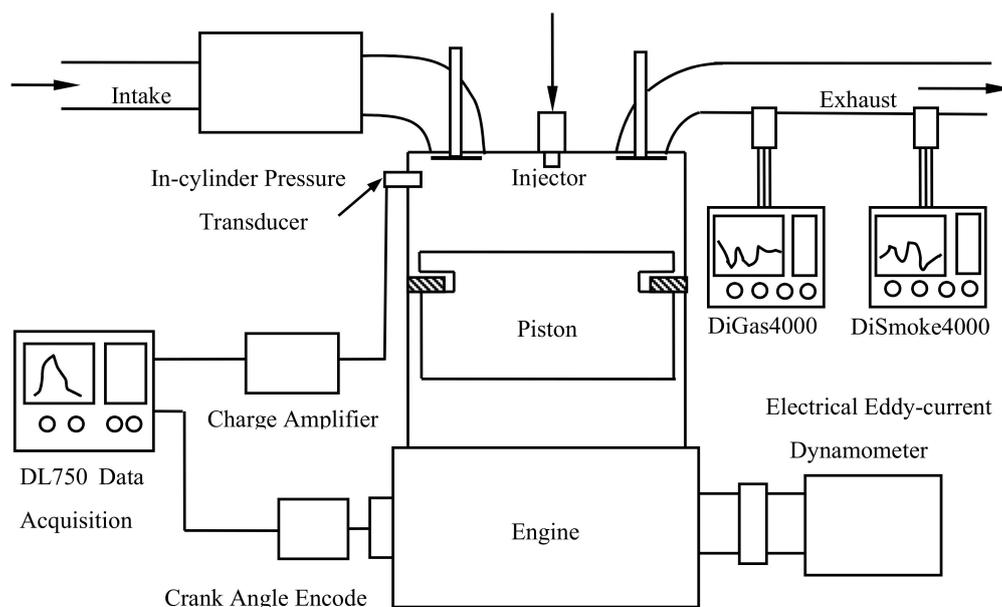


Figure 6. Experimental setup for engine tests.

4. Engine Test Results

Several kinds of biodiesel were developed in the past decade research activities. Except FAME, ethylene glycol monomethyl ether based biodiesels were focused. The effects on engine performance are digested and compared below. To know the full results, please refer to the corresponding references.

4.1. FAME

To compare with ethylene glycol monomethyl ether types of biodiesel, cottonseed oil methyl ester was prepared and used to study the combustion and exhaust emissions characteristics by 2102QB diesel engine.

When the engine fueled with this cottonseed oil FAME purely, its brake thermal efficiency improved to be 32.2% and 33.6% at the conditions of 70 N·m, 1400 r·min⁻¹ and 2200 r·min⁻¹, which are 29.6% and 30.0% for the petrodiesel operation, respectively.

Under 1400 r·min⁻¹ constant speed operating conditions, the exhaust smoke reduced by 30.0–47.4%; CO emissions reduced by 20.0–33.3% at 1400 r·min⁻¹; HC emissions decreased by 18.2–36.4%; and NO_x emissions decreased by 3.2–16.6%, respectively.

Under 2200 r·min⁻¹ constant speed operating conditions, the exhaust smoke reduced by 26.8–45.5%; CO emissions reduced by 33.3–50.0%; HC emissions decreased by 11.1–20.0% and NO_x emissions decreased by 13.1–24.2%, respectively.

4.2. Ethylene Glycol Monomethyl Ether Based Biodiesel

There were 5 vegetable oils used to react with ethylene glycol monomethyl ether to produce new model biodiesels. They are rapeseed oil, soybean oil, peanut oil, palm oil and cottonseed oil. The produced biodiesel can be named as Ethylene Glycol Methyl Ether X-oil Monoester. They have the same formula as RCOOCH₂CH₂OCH₃, where the “R” means different chain alkyl, which are provided in Table 1 (some). Their fuel properties can be checked in Table 3.

1. Ethylene Glycol Methyl Ether Rapeseed Oil Monoester [33,34].

The test engine was TY1100. Under the pure biodiesel operating conditions, the effects of biodiesel are as the following.

- Effect on Combustion

The combustion analyzed heat release rate shows that the ignition delay becomes 1.1 deg. CA shorter. Both the maximum heat release rate and peak cylinder pressure increase. The brake thermal efficiency was improved.

- Effects on emissions

Under full load operating conditions, smoke reduces 43.5–78.2%, the reduction of CO is 8.7–50% and HC is 11.4–61.5%, while NO_x a little increases.

2. Ethylene Glycol Methyl Ether Soyate Oil Monoester [38,39].

The test engine was TY1100. The tests were conducted mainly at 2300 r·min⁻¹ operating conditions. The engine ran on pure biodiesel of EGMMES and 50% biodiesel blended with petrodiesel by volume. The effects of biodiesel are as the following.

- Effects on energy consumption

For pure biodiesel operating conditions, the consumption increases by 16.9% while the energy consumption decreases by 7.9%, and for biodiesel and petrodiesel mixture operating conditions, the consumption increases by 1.4%, while the energy consumption decreases by 3.2%, respectively.

- Effects on emissions

For pure biodiesel operating conditions, smoke decreased from 54.7% to 85.7%, CO emission reduced up to 79.1% for the pure and 69.8% for its mixture operation. HC emission decreased by 61.6%. For biodiesel and petrodiesel 50% to 50% mixture operating conditions, smoke decreased from 46.5% to 83.3%, CO emission reduced up to 69.8%, HC emission decreased by 59.6%. Both fuels do not change NO_x emission significantly.

3. Ethylene Glycol Methyl Ether Peanut Oil Monoester [32].

The test engine was TY 1100. The test fuels were petrodiesel, peanut oil monoester biodiesel and their mixture at a proportion of 1:1 by volume. Most tests conducted under 1400 r·min⁻¹ and 2000 r·min⁻¹. The results were as the following.

- Effect on Combustion

The peanut oil monoester has high cetane number, leading to a little earlier auto-ignition than diesel. An improved engine thermal efficiency was observed when the engine fueled with the biofuel due to certain amount of oxygen contained in the new biodiesel. The peak cylinder pressure, pressure rise rate and the calculated heat release rate have no noticeable change.

- Effects on emissions

The exhaust smoke decreased by 25.0% to 75.0%, CO and HC emissions were lowered by the maximum of 50–70% and NO_x emission remained in the same level.

4. Ethylene Glycol Methyl Ether Palm Oil Monoester [40,41].

Smoke decreased by 69.0% to 89.3%. NO_x decreased about 25% at high speed conditions while increased 15% at low speed high load conditions. HC and CO emissions increased much (maybe mismarked, they should be decreased.)

5. Ethylene Glycol Methyl Ether Cottonseed Oil Monoester [42].

EGMECOM has a comparative high cetane number and oxygen content, which are the prime factors that determine its NO_x and smoke emissions, respectively.

EGMECOM, the combustion timing of engine is advanced, ignition delay is shortened, and the combustion is improved.

Compared to diesel fuel, a maximal reduction of the smoke, NO_x, CO, and HC are 50.0%, 50.0%, 20.0%, and 55.6%, respectively.

For convenient review, the test conditions and maximal reduction rate of emissions when using different biodiesel is summarized in Table 3. New model biodiesels are more significant than FAME in reducing smoke, HC and CO because of its higher CN and oxygen content. However new model biodiesels have a little influence in reducing NO_x except EGMEPOM (Palm) and EGMECOM. The different effects on engine emissions should be studied further.

Table 3. Effect of biodiesel on the reduction of engine emissions [32–34,38–42].

Fuel Type	Engine	Operation Condition	Smoke	HC	CO	NO _x
FAME	2102QB	1400 r·min ⁻¹	47.4%	36.4%	62.5%	16.2%
		2200 r·min ⁻¹	45.5%	20.0%	50.0%	24.2%
EGMEROM	TY110	2200 r·min ⁻¹	78.2%	61.5%	50.0%	Increase slightly
EGMESOM	TY110	2200 r·min ⁻¹	74.6%	61.6%	79.1%	changeless
EGMEPOM (Peanut)	TY110	1400 r·min ⁻¹	65.2%	53.8%	50.0%	changeless
		2000 r·min ⁻¹	75.0%	69.2%	50.0%	changeless
EGMEPOM (Palm)	2102QB	1400 r·min ⁻¹	58.3%	66.7%	60.0%	changeless
		2000 r·min ⁻¹	55.6%	66.7%	54.5%	32.2%
EGMECOM	2102QB	1400 r·min ⁻¹	50.0%	55.6%	A little	39.3%
		2000 r·min ⁻¹	45.5%	55.6%	A little	39.3%

4.3. Other Models of New Biodiesels

To study the effects of different biodiesel ether groups on engine combustion and emissions, different ether groups were selected and transesterified to biofatty acids, therefore, several kinds of biodiesels were prepared. Here listed are Ethylene Glycol Monoethyl Ether Soyate and Palm Oil Monoester, Ethylene Glycol propyl Ether Palm Oil Monoester, propylene glycol methyl ether palm oil monoester, diethylene glycol ethyl ether and triethylene glycol ethyl ether cottonseed oil Monoester were synthesized respectively. Their effects on engine combustion and emissions were digested below.

1. Ethylene glycol ethyl ether Soyate oil monoester

Compared with petrodiesel operation, when ran on pure biodiesel or their mixture, the engine power output remained the same level, while fuel consumption increased to some extent. This was thought to be unit heat energy remained due to the same product of decrease of LHV and increase of density.

When pure biodiesel operating, engine smoke reduced by 59.8–83.3%, CO reduction rate was 47.7–76.7% and HC decreased by 48.9–64.7%, while NO_x increased little. When 50% blending operation, engine exhaust smoke reduced 37.5–75%, CO reduced 13.9–55.8%, HC reduced 30.3–45.7%. NO_x reduced 50%.

2. Ethylene glycol ethyl ether palm oil monoester

The cylinder pressure analysis indicated that, the peak pressure reduced about 7% as well as the calculated heat release rate, while the ignition delay advanced 2.5 deg. CA. And engine brake thermal efficiency was improved for the fast combustion processes within the cylinder.

When diesel engine is fueled with this palm oil monoester, exhaust smoke reduced 36.5% to 60.0% when pure operation and 10% to 25% when the engine ran on the mixture of 25% blending with petrodiesel. Engine speed had a little effect on it. B100 made CO emission reduce 25% to 66%, HC reduce 44.4% to 55.6%, NO_x reduce 17% to 32.2% according to the engine load and speed, respectively.

3. Ethylene Glycol n-Propyl Ether Palm Oil Monoester [45].

With an increase of EGPEPOM in the blends, the peak cylinder pressure decreased while the start of combustion advanced. Meanwhile, the BSFC and brake thermal efficiency increased because of the low LHV and high oxygen content.

Smoke reduction was not significant when B25 operating, while B100 fueled operation, smoke reduced by 50% approximately. CO reduced 33.2% for B25 and 66.6% for B100. HC were 11% for B25 and 27.1% for B100. NO_x were reduced by 15.8% to 23.7% for B25 and B100 operating conditions.

4. Propylene glycol methyl ether palm oil monoester [44].

For the tested engine working under partial load mode, smoke emissions generally can be lessened by more than 50% and up to 75.0%. CO emissions can be reduced by 16.7% to 76.2%. HC emissions can be diminished relatively by 12.5% to 67.7%. NO_x emissions generally do not change.

5. DGMECOM [46].

Highest smoke reduction was about 60% and 80% at low load condition, about 40% and 45% at high load condition when b24 and b100 fuel applied respectively.

HC and CO changed irregularly, but were at the same level. NO_x reduced and affected with engine speed and load. High speed and load might result in significant 1/3 reduction in the test conditions.

The peak cylinder pressure decreased 1 or 2 bar, but combustion started earlier 2 or 3 deg. CA, the peak heat release rate moved forward and decreased, as a result the engine brake thermal efficiency changed a little high, correspondingly to the fuel ratios and operating conditions.

6. TGMECOM [47].

The combustion of TGMECOM was quite like DGMECOM, ignition delay was shorter and heat release rate decreased. The engine brake thermal efficiency and BSFC increased a little.

Smoke reduction rate was as high as 54.6%, NO_x reduced from 16.6% to 40%, CO reduced while HC increased all about 20% approximately.

The maximal reduction rate of emissions when using different biodiesel is summarized in Table 4. New model biodiesels have more obvious effects than FAME on reducing smoke and HC on account of

its higher CN and oxygen content. However new model biodiesels have a little influence in reducing NO_x and CO except EGEEESOM and PGMEPOM. The different effects on engine emissions should be studied further.

Table 4. Maximal reduction rate of emissions when using pure biodiesels [44–47].

Fuel Type	Smoke	HC	CO	NO _x
FAME	47.4%	36.4%	62.5%	24.2%
EGEESOM	83.3%	76.7%	64.7%	Increase slightly
EGEPEOM	60.0%	66%	55.6%	32.2%
EGnPEPOM	50%	66.6%	27.1%	23.7%
PGMEPOM	75%	76.2%	67.7%	changeless
DGMECOM	80%	33.3%	33.3%	33.3%
TGMECOM	54.6%	Increase 20%	20%	40%

5. Conclusions and Discussions

5.1. Ether Group Has Significant Effects on Fuel Properties

Ether group increases oxygen content and cetane number of the new model biodiesels, which meets the research purpose changing the fuel properties of biodiesels.

From Table 1, the density of petrodiesel, FAME and the new model biodiesels increases normally from 860, 880 and 910 approximately. Oxygen content changes from 10% to 14%. But their LHVs are generally in the same value, though lower than diesel. The higher density helps keep the engine power for most diesel engine fuel injection is valued in volume by compensating energy density. The shortage is their higher viscosity, which is more dispersing than its density and oxygen content, though there is no proof of bad effect on spray atomization, air fuel diffusion and finally its combustion.

5.2. Ether Group Has Significant Effects on Engine Combustion and Emissions

Fatty acid has an enough long chain, but FAME's cetane number is not so high for its unsaturated bonds. By introducing ether group, the CN of new model biodiesels increased to be 70, a big improvement compared to FAME of 50, in a simple way. Engine combustion analysis indicates the following factors: higher cetane number shortens the ignition delay time, which increases the temperature of air fuel mixture within the scope of spray; shorter ignition delay wakens premixing combustion and results in lower NO_x formation and emission; higher oxygen content decreases PM formation and emission; and both of higher CN and oxygen content together improve the biodiesel fuel combustion for the special chemical groups of ether and ester.

The developed new model biodiesels have higher potential to decrease smoke, NO_x, HC and CO than FAME. Most results indicated that FAME reduced smoke 30% to 50%, but the new model biodiesel reduced engine smoke as high as 80%. It also has significant reducing effects on NO_x, HC and CO. Concerning that the test engine was a type of Euro 1, further studies should be carried out with engines meeting euro 6 to make sure its potentials.

5.3. One Methyl Ether Group Is Important

The engine test results indicate that one methyl ether group is important to boost the biodiesel combustion properties. While ethyl ether, propyl ether and even poly ethylene glycol methyl ether do not show better performance than ethylene glycol methyl ether. This helps keep the price of new model biodiesels low, too.

5.4. Biodiesel Combustion Chemical Kinetics Should Be Studied

From the point of cetane number, fatty acid, FAME and the new model biodiesel, they have the same types of alkylchain, the difference is the transesterified ester or ethylene glycol methyl ether ester

group. Their CN improved much, so the effect on combustion should be investigated, as well as the mechanism of its effects on exhaust emissions.

Author Contributions: S.L. and H.G. conceived and designed the research topic by screening some of alcohols, ethylene glycol monomethyl ether was proposed. H.G. also designed the laboratory procedures for the new types of biodiesels transesterification processes. S.L. supervised the engine tests and data analyses of fuel properties and engine performances. W.C. wrote the text of the manuscript first and then the manuscript was revised and submitted by Z.Z. Z.Z., S.J. and T.R. took part in the data comparison with all the references.

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Abbreviations

AT	Autoignition Temperature/°C
BT	Boiling Temperature/°C
CA	Crank angle/(°)
CO	Carbon monoxide
CO ₂	Carbon dioxide
CN	Cetane number
CP	Cold Filter Plugging Point/°C
OS	Oxidative Stability
DOE	Department of Energy, US
DU	Degree of unsaturation
EGME	Ethylene Glycol Monoethyl Ether
FAME	Fatty acid methyl ester
EGMEROM	Ethylene Glycol Methyl Ether Rapeseed Oil Monoester
EGMESOM	Ethylene Glycol Methyl Ether Soyate Oil Monoester
EGMEPOM (Peanut)	Ethylene Glycol Methyl Ether Peanut Oil Monoester
EGMEPOM (Palm)	Ethylene Glycol Methyl Ether Palm Oil Monoester
EGMECOM	Ethylene Glycol Methyl Ether Cottonseed Oil Monoester
EGEESOM	Ethylene glycol ethyl ether Soyate oil monoester
EGEEPOM	Ethylene glycol ethyl ether palm oil monoester
EGnPEPOM	Ethylene Glycol n-Propyl Ether Palm Oil Monoester
PGMEPOM	Propylene glycol methyl ether palm oil monoester
DGMECOM	Di-ethylene Glycol Methyl Ether Cottonseed Oil Monoester
TGMECOM	Tri-ethylene Glycol Methyl Ether Cottonseed Oil Monoester
FTIR	Fourier Transform Infrared Spectroscopy
HC	Hydrocarbons
HCl	Hydrochloric acid
LHV	Lower Heating Value/(KJ/Kg)
K	Kalium; potassium
Na	Sodium
NO _x	Nitrogen oxides
OC	Oxygen Content/%
PM	Particulate matters

Appendix A

Table A1. FAME compositions and fuel properties [18–23,29].

Fatty Acids wt.%	Rapseed	Soybean	Vernicia Fordii	Cornus Wilsoniana	Idesia Polycarpa	Zanthoxylum Bungeanum	Xanthoceras Sorbifolia	Armeniaca Sibirica	Jatropha Curcas	Pistacia Chinensis	Elaeis Guineensis
C14:0	0.07	0.05	0.03	1.00							
C16:0	3.49	10.58	3.56	16.53	15.50	20.14	5.27	3.79	19.75	23.14	44.80
C16:1	0.00	0.00	0.97	6.65	0.30	0.67	0.99	0.30			
C18:0	0.85	4.76	2.62	1.77	1.39	0.15	1.92	1.01	4.63	1.18	3.80
C18:1	64.40	22.52	10.57	30.50	9.53	29.72	31.17	65.23	46.83	44.35	39.90
C18:2	22.30	52.34	14.64	48.50	64.81	29.62	44.47	28.92	28.50	28.51	9.28
C18:3	8.23	8.19	59.20	1.60	2.08	17.91	6.46	0.14	0.01	0.84	0.22
C20:0	0.10	0.20	0.09	0.17	0.10	0.35					
C20:1	0.90	0.04	0.48	0.12							
C20:3	7.27										
Others	0.73	1.61	8.51	0.05	1.53	3.24	0.89	0.03			
CP/°C	−4	−0.5	−11.0	0.0	−5.0	−6.0	−8.0	−14.0	0	−3.0	12.0
OS/h@110 °C	2.0	1.3	0.4	0.6	0.7	1.2	1.7	2.7	3.3	4.2	7.7
CN	52.9	50.9	37	49	45	46	47.6	48.8	51	51.3	62.0

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