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Application of Biodiesel in Automotive Diesel Engines

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Additional information is available at the end of the chapter

1. Introduction

1.1. background

Diesel engines due to the better fuel economy have been widely used in automotive area. However, the limited reserve of fossil fuel and deteriorating environment have made scientists seek to alternative fuels for diesel while keeping the high efficiency of diesel engine. Fuel consumption is expected to increase from 86 million barrels per day to 112 million barrels per day by 2035 according to the report published by US Energy Information Administration in 2011 [1]. The limited reserve cannot afford this usage. Another challenge is environmental deterioration and climate change. Excessive emissions of carbon dioxide (CO_2) to the atmosphere are regarded as the leading cause of global warming. In addition, other emissions, such as NO_x, SO_2, also have a close relationship with other forms of climate change, such as photochemical smog and acid rain. Due to these, the regulations on fuel economy and emission limits are increasingly stringent. Table 1 shows the EU emissions regulations for passenger cars came into force since 1992.

Tier	Date					HC+NO_x	
Euro 1†	Jul-92	2.72 (3.16)	-	-	-	0.97 (1.13)	0.14 (0.18)
Euro 2	Jan-96	1	-	-	-	0.7	0.08
Euro 3	Jan-00	0.64	-	-	0.5	0.56	0.05
Euro 4	Jan-05	0.5	-	-	0.25	0.3	0.025
Euro 5	Sep-09	0.5	-	-	0.18	0.23	0.005
Euro 6 (future)	Sep-14	0.5	-	-	0.08	0.17	0.005

Table 1. European emissions regulations for passenger cars (Category M*), g/km

However, it is not a long-term solution even though these measures can help alleviate or reduce the emissions and extend the lifetime of fossil fuel in industry, because one day fossil fuel would run out if the fuel consumption is kept at nowadays' rate. In addition, the decrease in fossil fuel reserve would lead to the increase of oil price. The rising fuel price raised the cost-competiveness of other energy sources, such as wind energy and solar energy. Hence some sectors, such as industrial and buildings, are driven towards other substitute energy sources when possible, whereas in transportation sector, liquid fuel is still the preferred choice. Consequently, the transportation share of the total liquid fuels increases in the projected period, accounting for 80% of the total increase in liquid fuel production [1].

Therefore, the efforts have been made to seek the alternative for fossil fuel, especially after the energy crisis in 1970s. People are trying to find a sustainable way to power the engines.

1.2. Biodiesel

Among the alternatives for fossil diesel, biodiesel has been widely investigated due to its renewability, comparable properties to fossil diesel and the reduction in main emission products.

Biodiesel is mainly comprised of mono-alkyl esters of long chain fatty acids and it was defined in standard ASTM D6751. Normally feedstock such as vegetable oil and animal fat is used to produce biodiesel through transesterification method.

With the on-going development of biodiesel, the categorization of biodiesel is developed. Generally biodiesel can be categorised by the readiness of feedstock and produce technologies. The biodiesel made from vegetable oil and animal fats using transesterification method is normally recognised as first-generation biodiesel. The second-generation biodiesel, Biomass to liquid (BTL) fuel is to turn cellulose into fuel components (enzyme fermentation or gasification through Fischer-Tropsch synthesis), and the feedstock theoretically can be any bio mass such as waste agriculture, wood chips etc. Some biodiesel from jatropha, algae, etc., despite being produced by transesterification method, is widely regarded as second-generation due to the technical challenge of feedstock planting and harvesting. Normally the second-generation biodiesel can supplement the drawbacks of the first-generation biodiesel particularly being non-competitive with food.

Different from above definition, another new fuel, Hydro-treated vegetable oil (HVO), using the same feedstock as 1st generation biodiesel, is viewed as second generation biodiesel, and BTL is third-generation [17]. The authors still categorize it into second-generation biodiesel because HVO shares the same feedstock with first-generation biodiesel even though it is made through different way and has better quality than first-generation biodiesel through transesterification.

1.2.1. History

Vegetable oil has been used in diesel engine long time ago. In 1900 after the invention of diesel engine,), Dr. Diesel used peanut oil to run one of his engines at the Paris Exposition of 1900. Vegetable oils were used in diesel engines until 1920s. The recent use of vegetable oil

as the alternative for diesel starts from early 1980s due to the concern about the energy supply. But biodiesel is not commercialised until late 1990s.For the direct use of vegetable oil, several difficulties occur, including the high viscosity, acid composition, free fatty acid content, and gum formation due to oxidation and polymerization during storage and combustion, carbon deposition, and oil thickening (Ma and Hana, 1999). Therefore, the direct use of vegetable oil may not be satisfactory and practical. The technologies to improve the vegetable oil appeared.

1.2.2. Production process

There are several ways used to produce FAME through vegetable oil, pyrolysis, cracking and transesterification. The common method is transesterification. Figure 1 shows the chemical reaction of FAME production. Triglycerides, the main component in vegetable oil and animal fat, reacts with alcohol in a caustic environment and produce Fatty Acid Methyl Ester (FAME) or Fatty Acid Ethyl Ester (FAEE) and the byproduct glycerol. As a result, biodiesel is a mixture of esters, small amount of glycerol, free fatty acids, partially reacted acylglycerol, and residual raw materials. Normally methanol is used for the reaction for the higher reaction rate and lower price. The fuel qualities may be varied in terms of alcohol used. Methyl ester was better than ethyl ester from the point of engine performance: higher power and torque could be achieved.
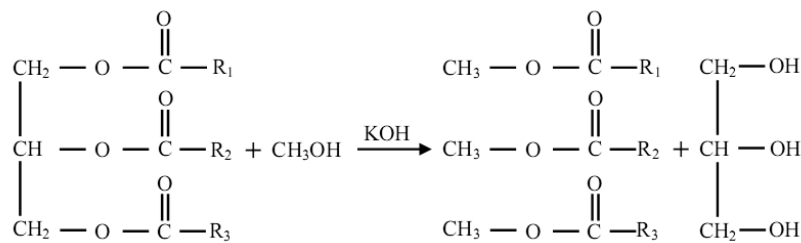

Figure 1. Transesterification reaction in caustic environment

Different from transesterification, Hydro-treating of vegetable oil or animal fat (HVO) have been developed by several companies, such as Neste Oil, Axens IFP, and Honeywell UOP. In the hydro-treating process, vegetable oil or animal fat is also the feedstock. Hydrogen is added into the plant to remove the oxygen content and saturate the C=C and the final products are paraffin, propane, water and CO_2. Propane is also a promising and valuable fuel product. Due to the excellent properties,

$$\text{Triglycerides} + H_2 \xrightarrow[\text{Catalyst}]{} \text{Green diesel} + H_2O/CO_2 + \text{Propane}$$
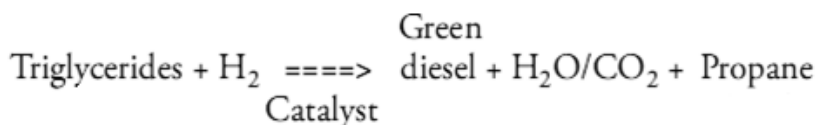
Figure 2. Product routes of transesterification and hydro-treated method

Fischer-Tropsch (FT) method is another way to produce synthetic fuel, using various ligno-cellulosic feedstock. BTL (biomass-mass-to-liquid) fuel, GTL (Gas-to-liquid) fuel, and CTL (Coal-to-liquid) fuel are produced with this method. GTL and BTL are not sustainable fuels for natural gas and coal are not renewable. However, in this chapter GTL is included later because it shares the similar production process and has similar physiochemical properties with BTL. Figure 3 shows the manufacturing process of FT synthetic fuel. The solid feed-stock (coal and biomass) are initially gasified, then the composition of the syngas and CO_2 and sulphur compounds are removed before the synthesis process. After the synthesis process, the products are refined and the refined products includes the synthetic diesel and gasoline blendstock.
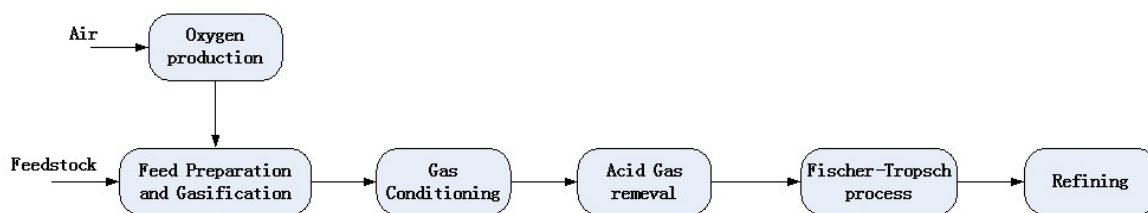
Figure 3. FT fuel manufacturing process

1.3. Biodiesel standards

Due to the difference in the feedstock and manufacturing process, the FAME products may vary very much. Table 2 lists several main standards used in the world, aiming at reach the satisfaction and the equipment compatibility.

Bio-Diesel	Unit	Austrian Standard C1190 Feb. 91	Australian Bio-diesel Standard	DIN 51606 (1997/9/1)	U.S. Quality Specification NBB/ASTM	Euro Standard EN 14214
Density at 15°C	g/cm3	0.86 - 0.90	0.86 – 0.89	0.875 - 0.90	/	0.86 - 0.90
Viscosity at 40°C	mm2/s	6.5 - 9.0 (20°C)	3.5 – 5.0	3.5 - 5.0	1.9 - 6.0	3.50 - 5.00
Flash point	°C	Min. 55	120.0°C	Min. 110	Min. 100	Min. 120
	(°F)	-131		-230	-212	-248
CFPP	°C (°F)					
	summer	Max. 0 (32)	/	Max. 0 (32)	/	
	winter	Max. -8 (17.6)		Max. -20 (-4)		
Total sulphur	mg/kg	Max. 200	Max. 50 mg/kg	Max. 100	Max. 500	Max. 10.0
Conradson (CCR) at 100% at 10%	% mass	Max. 0.1	Max 0.05	Max. 0.05	Max. 0.05	/
		/	Max 0.30	/	/	Max. 0.30

Cetane number	-	Min. 48	Min. 51	Min. 49	Min. 40	Min. 51
Sulfated ash content	% mass	Max. 0.02	Max. 0.02	Max. 0.03	Max. 0.02	Max. 0.02
Water content	mg/kg	free of deposited water		Max. 300	/	Max. 500
Water & sediment	vol. %	/	Max. 0.05	/	Max. 0.05	/
Total contamination	mg/kg	/	Max. 24	Max. 20	/	Max. 24
Copper corrosion (3 hs, 50°C)	degree of Corrosion	/	< 10mg/kg sulphur – 1 "/ 10mg/kg sulphur – 3 max ——1		No. 3b max.	1
Neutralisation value	mg	Max. 1	/	Max. 0.5	Max. 0.8	Max. 0.50
Oxidation stability	h	/	Min 6 @ 110°C	/	/	Min. 6.0
Methanol content	% mass	Max. 0.30	0.2	Max. 0.3	Max. 0.2	Max. 0.20
Ester content	% mass	/	Min 96.5	/	/	Min 96.5
Monoglycerides	% mass	/	/	Max. 0.8	/	Max. 0.80
Diglycerides	% mass	/	/	Max. 0.4	/	Max. 0.20
Triglycerides	% mass	/	/	Max. 0.4	/	Max. 0.20
Free glycerine	% mass	Max. 0.03	Max. 0.02	Max. 0.02	Max. 0.02	Max. 0.02
Total glycerine	% mass	Max. 0.25	Max. 0.25	Max. 0.25	Max. 0.24	Max. 0.25
Iodine value		/	/	Max. 115	/	Max. 120
Linolenic acid ME	% mass	/	/	/	/	Max. 12.0
Polyunsaturated ("/ =4db)	% mass	/	/	/	/	Max. 1
Phosphorus content	mg/kg	/	Max. 10	Max. 10	/	Max. 10.0
Alkaline content (Na +K)	mg/kg	/	/	Max. 5	/	Max. 5.0
Alkaline earth metals (Ca + Mg)	mg/kg	/	/	/	/	Max. 5.0

Table 2. Biodiesel Standards

1.4. Pros and Cons

The following summarised the advantages of biodiesel:

• Renewable energy source in comparison with traditional fossil fuel

• Degradability

• Much less sulphur, leading to lower toxic substances in the exhaust

• Absence of PAHs and around 10% of oxygen help the reduction of HC and CO

• Various feedstock

The use of bio-diesel fuels cannot occur without adopting a series of precautions. Indeed, unless the proper precautions are taken, biodiesel fuels can cause a variety of engine performance problems including filter plugging, injector coking, piston ring sticking and breaking, seal swelling and hardening/cracking and severe lubricant degradation. Bio-diesel also requires special treatment at low temperatures to avoid an excessive rise in viscosity and loss of fluidity.

Long-term storage problems can be observed as result of the poor oxidation stability of bio-diesel fuels. Thus additives may be needed to improve storage conditions. Furthermore, bio-diesel is an excellent medium for microbial growth. As water accelerates microbial growth and is more prevalent in biodiesel than in petroleum based fuels, special care must be taken to remove water from fuel storage tanks to avoid operational problems such as sediment build-up, premature filter plugging or storage tank corrosion.

1.5. Security of supply

Another reason for the search of alternative fuel is the energy security. The economical growth can promote the demand for energy. Table 3 listed crude oil reliance on imported oil of US and China. The reliance of the two countries are up to 44.8% and 56.54%, respectively. The energy supply can be well alleviated if biodiesel can be produced and used in commercial scale. Further analyses are needed to understand the fuel difference and can help fuel design during the biodiesel production process. The Commission Green Paper (CEC, 2000) reported an ambitious EU programme on the usage of biodiesel that 20% alternative fuel substitution by 2020 in conventional fuel in the road transport sector is set. On another hand, the utilisation of biodiesel leads to concerns of land use, deforestation and negative effect on bio-diversity needs further exploration.

	Year 2007	Year 2008	Year 2009	Year 2010	Year 2011
US[1]	58.2%	57.0%	51.5%	49.2%	44.8%
China	47.2%	49.8%	52%	54.8%	56.5%

Table 3. [1] US Department of Energy, Energy Information Administration, Monthly Energy Review, Washington, DC, March 2012, Table 3.3aCrude oil reliance of US and China from 2007 - 2011

2. Fuel properties

2.1. Fuel composition

Due to the various feedstocks for biodiesel, the fuel composition varies in a wide range. Generally the fats and oils contain 10 common types of fatty acid consisting of 12- to 22-carbon chain, and over 90% are between 16- and 18-carbon chains [11]. Table 4 shows the composition of some common FAME. Some of these are saturated, some are monounsaturated and others are poly-unsaturated. The composition of biodiesel determined the chemical and physical properties, such as the fuel viscosity, surface tension, cetane number (CN),

oxidation stability, low-temperature properties, as well as the following combustion and emission characteristics.

2.2. Viscosity

Viscosity is a measure of resistance to flow of a liquid due to internal friction and it is one of the most important parameters in evaluate the fuel quality. Viscosity affects engine working process very much. Higher viscosity would prohibit atomisation and instability of fuel droplets, and promote the formation of deposit. This also explains why neat vegetable oils have difficulty when used in diesel engines directly. The viscosity can be measured according to the standards such as ASTM D445 or ISO 3104. The viscosity of individual saturated fatty acid ester increases with carbon chain length and non-linearly decreases with the increase of number of double bonds [4]. In addition, the position of C=C double bond and the branching in the ester moiety has less effect on viscosity. Biodiesel has a higher viscosity than fossil diesel. At lower blend ratio, the viscosities of diesel and biodiesel/diesel blend are very close. As the blend ratio continues to increase, biodiesels show a much higher value. This can partly explain why biodiesel/diesel blends with lower blend ratio are widely used in diesel engines.

		Rapeseed (high erucic)	Rapeseed (low erucic)	Soybean	Sunflower	Coconut oil	Palm kernel oil	Palm oil (Africa)	Palm oil (Indonesia)	Beef tallow	Chicken fat	Fish oil
Saturated fatty acids	< C10:0					~13	~7					trace
	C12:0	trace	trace			41-46	41-45	trace	trace-0.5	trace		trace
	C14:0	trace	trace	<0.5	trace-0.1	18-21	15-17	1-2	~1	2-4	~1	6-9
	C16:0	2-4	3-6	8-12	5.5-8	9-12	7-10	41-46	41-47	23-29	20-24	11-20
	C18:0	1-2	1-2.5	3-5	2.5-6.5	2-4	2-3	4-6.5	4-6	20-35	4-7	1-4
	C20:0	0.5-1	<1	<0.5	<0.5	trace	trace-0.3	~0.5	~0.5	<0.5		trace-1
	C22:0	0.5-2.0	trace-0.5	trace	0.5-1.0	trace	trace-0.5			trace		trace
	C24:0	0.5	trace-0.2		<0.5							trace-1
Unsaturated fatty acids	C14:1					trace				~0.5		trace
	C16:1	~0.5	0.1-0.5	trace	<0.5	trace		<0.5	~0.5	2-4	~7	6-11
	C18:1	11-24	52-66	18-25	14-34	5-9	10-18	37-42	37-41	26-45	38-44	12-15
	C18:2	10-22	17-25	49-57	55-73	0.5-3	1-3	8-12	~10	2-6	18-23	1-2
	C18:3	7-13	8-11	6-11	trace-0.4	trace	trace-0.5	trace-0.5	trace-0.5	~1	~1	0.5-1
	C20:1	~10	1.5-3.5	<0.5	<0.5	trace	trace-0.5	trace	trace	<0.5		1-16
	C20:x*		trace-0.1							trace		6-19
	C22:1	41-52	trace-2.5		trace-0.3							1-20
	C22:x*									~0.5	0.5-1	5-14
	C24:1		trace									trace-1
Other constituents	Phosphatides	2.5		1.1-3.2	<1.5			0.05-0.1		<0.07		
	Tocopherols	0.07-0.08		0.09-0.12	0.07-0.1	0.003		0.02-0.12		0.001		
	Sterols	0.5-1.1		0.2-0.4	0.25-0.45	0.05-0.1	0.08-0.12	0.04-0.08		0.08-0.14		~0.3

* x > 1
trace ≤ 0.05%

http://www.dieselnet.com/tech/fuel_biodiesel_app.html

Table 4. Composition of common FAME.

2.3. Cetane number (CN)

CN is used to evaluate fuel ignition quality determined by the time between start of injection and start of combustion. Higher CN indicates shorter time after the injection. CN is mainly determined by the fuel composition and can affect engine startability, noise and

emission characteristics. Generally, biodiesel has a higher CN than mineral diesel. This can be attributed to the longer carbon chain length of biodiesel. Unsaturation and carbon chain length are the most two influential factors of CN [16, 12, 22]. Higher saturation degree and longer fatty acid chain length can lead to a lower CN. The positions of chemical group may also influence the CN. The CNis the highest when the carbonyl group is at the end of the carbon chain and lowest in the middle of the carbon chain. In addition, a higher level of hydroperoxides increases CN and a shorter chain length of the alcohol moiety may also increase CN [12, 22].

2.4. Low-temperature property

Diesel engines may encounter the start-up and performance problems at low temperatures. As ambient temperatures decrease towards the fuel saturation temperature, high-molecular-weight compound begin to nucleate and form was crystals. The existence of was crystals may affect the fuel supply and engine performance. Three parameters, cloud point (CP), pour point(PP), and cold filter plugging point (CFPP) are used to describe low-temperature properties. The temperature at which crystals become visible is called CP because the crystals lead to a cloudy suspension. if the temperature continues to decrease, the crystals would fuse together and form larger agglomerates. The temperature at which crystal agglomeration is large enough to prevent free pouring of fluid is called PP. A more complicated test procedure is involved in order to obtain CFPP. The test uses a vacuum to draw a 20 cc fuel sample through a 45 micron screen within a 60 seconds. The lowest temperature that the fuel can still flow through the filter is called CFPP.

This is an very concerning issue in application of biodiesel into diesel engines. Neat biodiesel has poorer low-temperature performance than conventional diesel. Therefore, when biodiesel is used in cold condition, the biodiesel crystafdl may block the fuel pipe and the fuel filter, and even abrade the high-pressure fuel pump, shorting the lifetime of vehicle engines. Research has shown that the cold flow property is associated with the saturated FAME in vegetable oil based biodiesel. The higher the proportion of saturated FAME and the longer chain FAME in saturated FAME, the poorer the cold temperature performance is [31].

Generally, the low-temperature properties can be improved by following methods:

- Blending with fossil diesel
- blending with additives
- Crystallization fractionation by decreasing the saturated alkyl ester content in the biodiesel.
- Employing branched esters

3. Application in Diesel Engines

The engine performance fuelled with biodiesel is crucial for the application of biodiesel. The mainly involved problems may include corrosion, material degradation, injector coking, fil-

ter plugging and piston ring sticking, engine deposits etc. therefore, in the following section, the studies focusing on these issues were introduced.
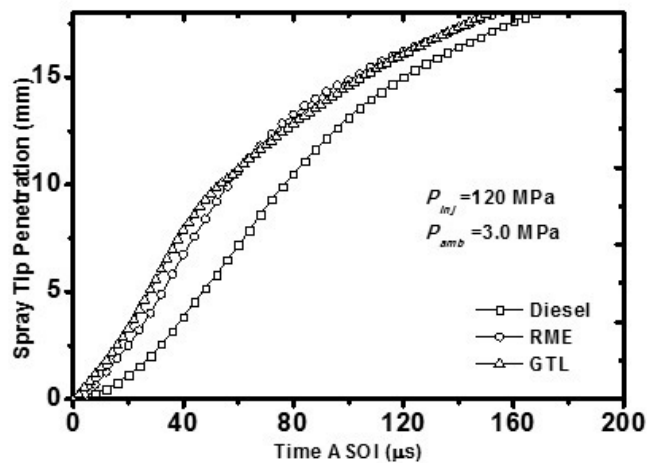
3.1. Fuel spray characteristics

Injection spray is the process that fuel is injected from nozzle, and it is associated with following fuel atomisation, interaction with surrounding gas, mixture formation and combustion. Regarding to a new fuel applied into the diesel engine, the spray process is different due to the different properties from diesel, and the control strategy should be changed accordingly in order to achieve the optimum performance. Viscosity, surface tension and density are the three main parameters, which influence fuel spray characteristics. Higher viscosity and surface tension will prohibit the atomisation and instability of fuel droplets. Due to the different biodiesels properties from diesel, studies on the spray characteristics are necessary.

3.1.1. Near-field spray characteristics

In the near-field of nozzle, the spray is dominated by the injection dynamics while the spray is affected by the ambient conditions in the far field. According to Hiroyasu's model, before the $t_{breakup}$, which represents the time for fuel jet breakup, the penetration length is proportional to the time after start of injection, namely ASOI. However, the non-linear phenomenon has been observed by a number of researchers. The acceleration process has been found to be different among fuels. Figure 4 compares the morphology of the spray process of the three tested fuels, ULSD, RME and GTL and Figure 5 shows the spray tip penetration length evolution after start of injection (ASOI) using an ultrahigh-speed CCD camera of up to 1 million shots per second. The initial non-linear penetration can be observed, indicating the acceleration period at the initial spray stage. GTL fuel has longer penetrating length than RME and diesel even though it was overtaken by RME 70 μs ASOI. Several publications have reported that GTL with lower density has a shorter penetration delay. However, these were based on the global fuel spray characteristics using a relatively low speed camera [21, 13]. The temporal resolution is not high enough to capture the near-field spray process.
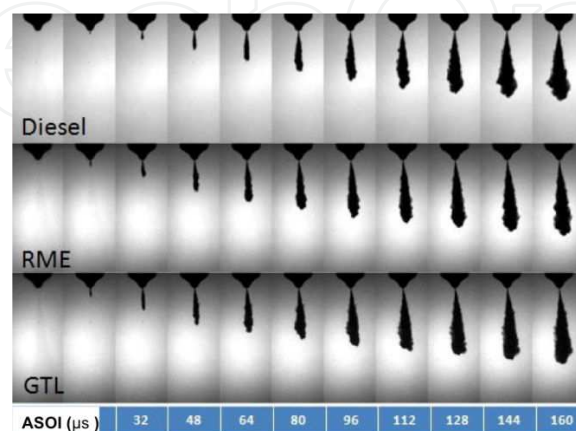
Figure 4. Sequence of spray images in a single time-resolved ULSD spray (Pinj=120 MPa, P_{amb} =3.0 MPa and t_{dur}=1.5 ms)

Figure 5. Spray tip penetration length evolution against time ASOI (P_{inj}=120 MPa, P_{amb} =3.0 MPa and t_{dur}=1.5 ms)

3.1.2. Macroscopic spray characteristics

Normally, biodiesel shows a longer penetration and narrower spray angle than fossil fuel due to the higher viscosity, surface tension and density. The penetration length of biodiesel increases with the blend ratio, higher biodiesel content requires longer breakup time [15]. The difference between the two type fuels can be varied at different conditions. Senatore et al. [24] experimentally studied biodiesel spray characteristics at different ambient pressures. The authors showed that little difference can be observed at the ambient pressure of 1.2 MPa while the penetration length significantly increased in contrast to diesel spray at the ambient pressure of 5.0 MPa. In addition, biodiesel may have a lower penetration velocity due to the negative effect of fuel density on spray velocity [9].

### 3.1.3. Sauter Mean diameter (SMD)

SMD is one of the parameters to evaluate fuel atomisation quality and represents the ratio of total droplet volume to surface area. Smaller SMD indicates more small fuel droplets and the larger contact area with surrounding gas. Due to the high viscosity and surface tension, SMD of biodiesel is higher than fossil diesel. Allen et al. [3] conducted the comparative analysis on 15 biodiesels and a larger SMD, between 5%-40%, can be observed and concluded an empirical equation to estimate SMD:

$$SMD = 0.002103\mu + 0.000330\sigma \qquad (1)$$

where μ is fuel dynamic viscosity (Pa.s) and σ is fuel surface tension (N/m).

Figure 6 compared diesel with neat RME and GTL at different injection pressure along the spray axis in terms of SMD. It can be seen that the injection pressure has a significant impact on droplet size. The SMD decreases dramatically when the injection pressure increases from 80 MPa to 120 MPa. GTL has the lowest SMD among all the three measured fuels at the giv-

en conditions while RME has the largest droplet size. The SMD evolution also decreases with the increase of the axial distance downstream of the nozzle even though there is a slightly increase from 40 mm to 50 mm at the 80 MPa condition. This may be caused by the droplet coalesce.
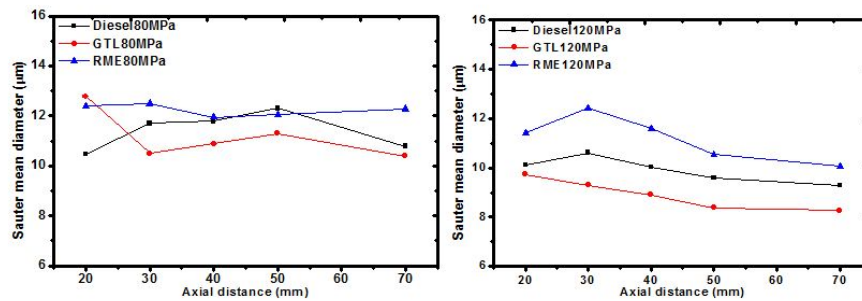
Figure 6. SMD distribution along the spray axis under injection pressure of 80 MPa (Left) and 120 MPa (Right)

3.1.4. Wear Performance and Durance

In diesel engines, the engine parts are lubricated by the fuel itself. In order to meet diesel engine emission standards, Ultra-low sulphur diesel (ULSD) are produced, which has a maximum sulphur content of 15 ppm. However, the relatively poor lubricity of ULSD may lead to the failure of engine parts, such as fuel pumps and injectors. The inherently greater lubricity of Biodiesel can offset the drawback of ULSD, and a small percentage of biodiesel can restore the lubricity of diesel [28].

It is also necessary to study the engine endurance in order to fully apply biodiesel into vehicle operation. Graboski et al. [14] reviewed previous studies and concluded that nitrile rubber, Nylon 6/6 and high-density polypropylene exposed to methyl soyester and D-2 blends exhibited changes in physical properties and fluorinated elastomer must be adopted for biodiesel application. Terry et al. [30] examined the durability of a set of five commonly used elastomers in automotive fuel systems in different biodiesel blends (B5 and B20) and the effect of a highly oxidized biodiesel blends on the elastomers was studied. The results demonstrated that it appeared to be compatible with these elastomers, for highly oxidized and unoxidized B5 and unoxidized B20, but B20 prepared from highly oxidized biodiesel shows the potential for significant problems.

3.2. Engine Output performance

The adaptability of biodiesel in diesel engines has been well studied from low blend ratio to neat biodiesel. Due to the potential damage of biodiesel on vehicle, normally biodiesel blended with diesel were mostly studied. In general, typical heating value for biodiesel is lower than that of fossil diesel. A greater amount of fuel is subsequently required to maintain the same engine output. Greater fuel consumption of up to 13% with heavy-duty engines over the United States Federal Test Procedure (US-FTP) cycle was observed. Due to

the lower heating value, engine power loss is expected and the loss increases with the blend ratio of biodiesel in diesel [25, 33]. Figure 7 shows the output power of an 4-cylinder common-rail diesel engine with different biodiesel blends at two engine speeds. With the increase of biodiesel blend concentration, maximum out power was gradually reduced, especially in the higher blend ratio. Figure 8 presents the brake specific fuel consumption (BSFC) corresponding to the condition of Figure 7. The obvious increase in fuel consumption has been observed using higher biodiesel/diesel blends. From Figure 7 and Figure 8, it can be found that the output performance and fuel economy of biodiesel/diesel blends are very close to those of diesel when the blend ratio is under 20%. Therefore, biodiesel/diesel blends with lower blend ratio are preferred.
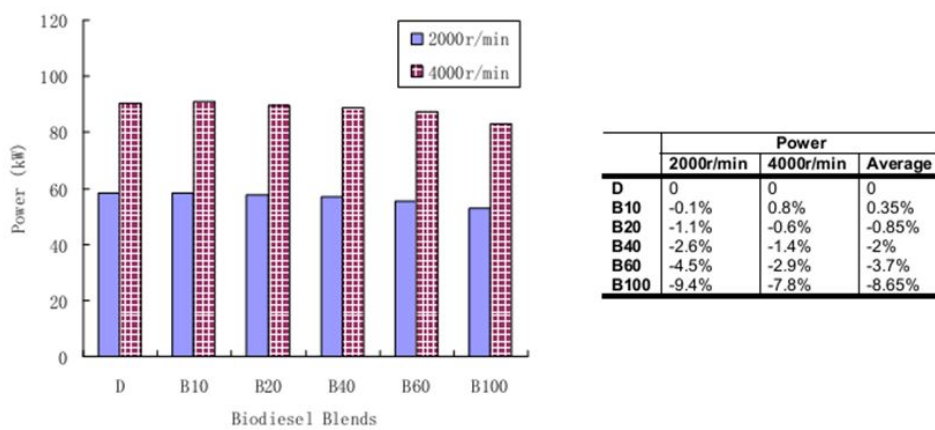

	Power		
	2000r/min	4000r/min	Average
D	0	0	0
B10	-0.1%	0.8%	0.35%
B20	-1.1%	-0.6%	-0.85%
B40	-2.6%	-1.4%	-2%
B60	-4.5%	-2.9%	-3.7%
B100	-9.4%	-7.8%	-8.65%

Figure 7. Output power of different biodiesel blends at two speeds [33]

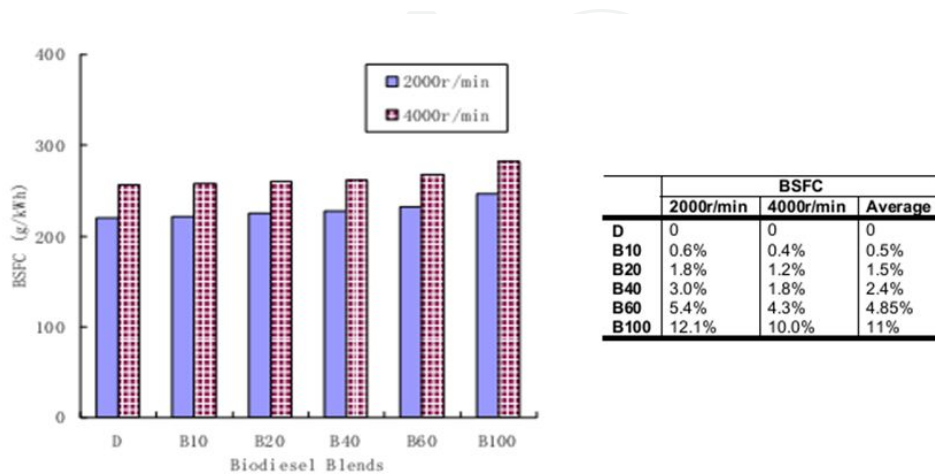|	BSFC		
	2000r/min	4000r/min	Average
D	0	0	0
B10	0.6%	0.4%	0.5%
B20	1.8%	1.2%	1.5%
B40	3.0%	1.8%	2.4%
B60	5.4%	4.3%	4.85%
B100	12.1%	10.0%	11%

Figure 8. BSFC of different biodiesel blends at two speeds [33]

3.3. Combustion characteristics

In diesel engines, combustion is to release energy contained in fuel, then impart work on piston, and power the engine. Factors affecting combustion characteristics include fuel properties and in-cylinder conditions. Biodiesel has a higher CN and the effect of CN on combustion has been discussed in previous section. The average peak cylinder pressure increases when biodiesel or its blends are used. For the application of biodiesel into diesel engines, advanced injection timing and increased injection pressure have been normally used. This is due to their differences in density and bulk modulus of compressibility. Combustion and emissions characteristics have been investigated by Chuepeng et al. [7] using different RME blends from B0 to B50 in a single-cylinder diesel engine in terms of engine load, EGR (Exhaust gas recirculation), and injection timing. At the same engine load, the proportion of fuel burnt in the premixed phase increases and the start of combustion is advanced as the proportion of RME in ULSD increases. With the same operating conditions, increase in EGR rate of up to 20%, slightly reduces the peak pressure and increases ignition delay.

3.4. Emissions

3.4.1. Regulated emissions

A number of studies on the engine emissions of engines powered by biodiesel or blends have been carried out. Environmental Protection Agency (EPA) in the United States correlated the biodiesel ratio with the changes in pollutants using statistical regression analysis and also the average effect of biodiesel on heavy-duty diesel engines [10]. The NO_x emissions increased with the concentration of biodiesel and the increase is by 10% at B100 while HC, CO and PM were greatly reduced. The significant reduction of emissions of HC, CO and PM can be attributed to the oxygen content in biodiesel.

It has been widely reported that NO_x increases as biodiesel is used in diesel engines. A number of efforts have been made in order to understand the formation mechanism and eliminate this penalty. There are several main reasons have been suggested:

- Advanced injection timing

- Oxygen content in biodiesel

- Double bond

- Radiative heat transfer

- Higher adiabatic flame temperature

An advanced injection timing due to the higher bulk modulus of biodiesel in pump-in-line injection system leads to the earlier start of combustion, resulting in higher in-cylinder temperature, which can increase NO_x emission [29, 2]. However, it is well understood that advanced injection timing increases NO_x emission in diesel engine [20], and this seems not to be the main contribution to NO_x increase as broad application of common rail injection system, which can well control the injection timing. Schmidt et al. [23] experimentally studied

the effect of concentration of oxygen in intake gas on NO_x emission, and found that NO_x emission increases with the oxygen content in mixture. However, the effect of oxygen content in air on combustion is different from that of oxygen content in biodiesel itself. The radiative heat transfer may also play a role in the NO_x increase. Soot radiation is the primary way of heat loss from in-cylinder flame and biodiesel can reduce this heat loss and will increase the flame temperature and produce more NO_x [6]. The double bond in biodiesel composition is another potential to increase NO_x emission. The double bonds lead to higher adiabatic flame temperature, and the biodiesel with higher unsaturated ester percentage corresponded to higher NO_x emission [27, 19]. Ban-Weiss et al. [5] also revealed that slight difference in the adiabatic flame temperature can lead to a measurable increase in NO_x. Mueller et al. [20] suggested that NO_x increase in biodiesel-fuelled engine is the result of a number of mechanisms, and the relative importance of each mechanism may vary under different operating conditions and indicated that air/fuel mixture close to stoichiometric at ignition and in the standing premixed auto-ignition zone near flame lift-off length may be the key factors in explaining the NO_x increase, whose effect could cause higher local and average in-cylinder temperature and lower radiative heat losses.

Therefore, three main strategies to alleviate the NO_x emission can be proposed: one is to determine the biodiesel compound that can lower NO_x emission or use a proper base fuel and additives, another is to design the combustion system to prohibit NO_x production by lower the combustion temperature, and the third one is to recalibrate the engine by tuning the injection strategy.

3.4.2. Unregulated emissions

For other unregulated emissions from an engine fuelled with biodiesel, polycyclic aromatic hydrocarbon (PAH) and nitro PAH compounds are substantially reduced, as well as the lower levels of some toxic and reactive HC species [26]. The PM composition (i.e. volatile material and elemental carbon) from the combustion of RME-based biodiesel blend (B30) in a turbo-charged engine with EGR operation was studied using thermo-gravimetric analysis (TGA) [8]. Generally, total PM mass from B30 combustion was lower than that for diesel in all engine operating conditions. Elemental carbon PM mass fractions were slightly lower for the B30. The volatile material portions of the B30 particulates are greater than those of diesel particulates irrespective of engine operating condition. For both fuels used in the test, volatile material was observed to be higher at idle speed and light load when exhaust emissions were at low temperature.

In previous regulations on PM, mass is the only concern. With the increasing concern on exhaust emissions, the PM size and number are to be limited by future emission regulations. [32] studied the particulate matter characteristics of RME10 and GTL10. It was found that the application of RME10 and GTL10 leads to a reduction in both total particle number and non-volatile part number over the test conditions. The obtained images from SEM (Scanned Electronic Microscopy) for the three test fuels are shown in Figure 9. The images show the morphology of PM at two magnifications. The authors found that PM from diesel combustion has more clusters than those from RME10 and GTL10 from Figure 10 (a), (c) and (e), indicating that primary particle size of the tested fuels is around 20 mm Figure 10. (b), (d) and (f).
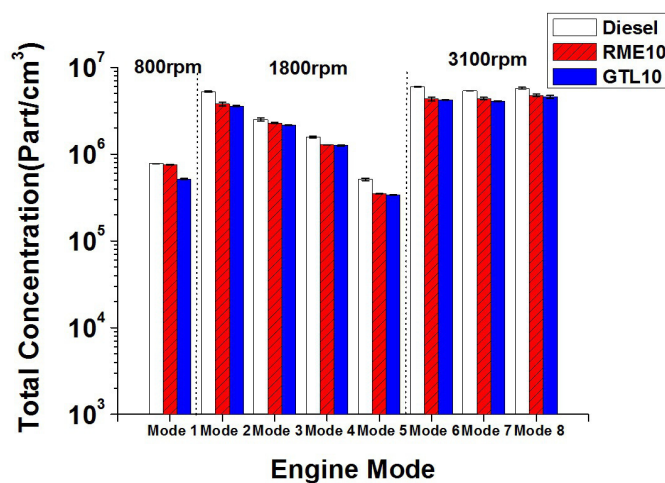
Figure 9. Exhaust particulate number concentration (total)
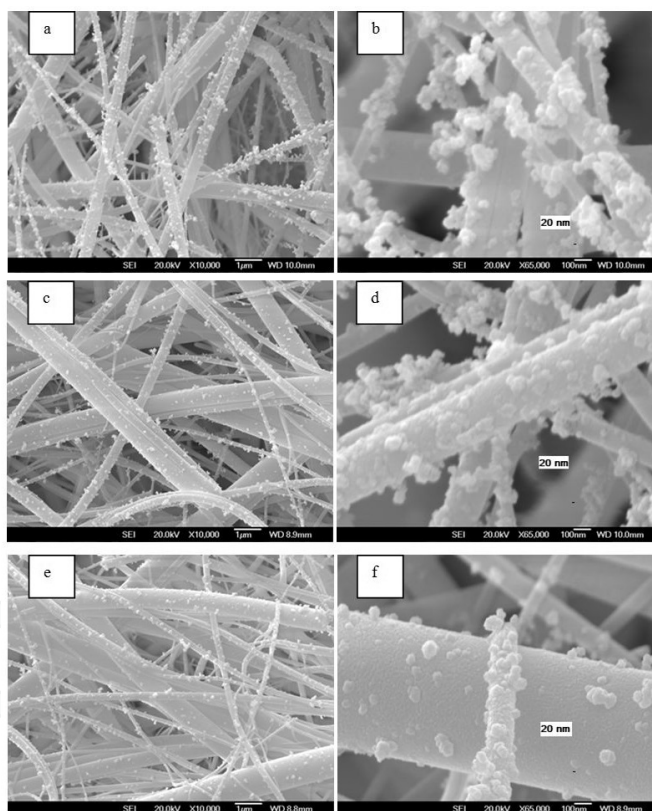

Figure 10. Particle morphology (captured under engine mode of 1800 rpm, 30 Nm): (a) Diesel magnification of 10000; (b) Diesel magnification of 65000; (c) RME 10 magnification of 10000; (d) RME magnification of 65000; (e) GTL10 magnification of 10000; (f) GTL10 magnification of 65000

3.5. Engine emission optimisation

Two popular methods have been used to reduce the engine out emission for biodiesel-fuelled engines: injection strategy and EGR. For the former, the combustion process can be controlled by injection timing and injection pressure. For the time being, the common rail injection system has been widely used and multiple injections up to of 5 times can be realised. Through this way, the fuel injection rate is controllable. The NO_x can be reduced through pre-injection with small amount fuel; this prevents a long period of ignition delay and therefore leads to a lower peak pressure; for the latter, EGR is always an effective way to reduce NO_x emission. Due to the induction of exhaust gas, the global in-cylinder temperature is reduced, avoiding the thermal conditions favoured by NO_x formation. Ladommatos et al. [18] also revealed that the reduction in combustion temperature is a consequence of the reduced peak rate of the premixed phase combustion due to the lower oxygen availability.

4. Conclusions

Biodiesel is the most promising fuel in the near future as an alternative to fossil diesel. Despite of its advantages, it still has some disadvantages such as source for massive feedstock, relatively poor low-temperature properties, increase in NO_x emissions, etc. These issues should be sorted out before biodiesel is applied into diesel engines in a large scale. Therefore, in-depth studies on the application of biodiesel into diesel engines are necessary. The research on alternative feedstocks is also an important area and the second-generation biodiesel is more promising made from algae and the genetic modification is a potential way to solve this problem of source of massive feedstock. The low-temperature fuel properties can be improved by additives or the production routine. In addition, diesel engines should also be optimised in order to achieve the optimal performance and emissions.

Abbreviations:

ASOI	After start of injection
BTL	Biomass-to-liquid
BSFC	Brake specific fuel consumption
CCD	Charge-coupled device
CN	Cetane number
CO	Carbon monoxide
CTL	Coal-to-liquid
EPA	Environmental Protection Agency
FAME	Fatty acid methyl ester
GTL	Gas-to-liquid

HC	Hydrocarbon
HVO	Hydro-treated vegetable oil
NOx	Nitric oxide
PAH	Polycyclic aromatic hydrocarbon
RME	Rapeseed methyl ester
ULSD	Ultra-low sulphur diesel

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