

Engine Performance Characteristics for Biodiesels of Different Degrees of Saturation and Carbon Chain Lengths

P.X. Pham
The University of Sydney

T.A. Bodisco, S. Stevanovic and M.D. Rahman
Queensland University of Technology

H. Wang, Z.D. Ristovski and R.J. Brown
Queensland University of Technology

A.R. Masri
The University of Sydney

ABSTRACT

This experimental study examines the effect on performance and emission outputs of a compression ignition engine operating on biodiesels of varying carbon chain length and the degree of unsaturation. A well-instrumented, heavy-duty, multi-cylinder, common-rail, turbo-charged diesel engine was used to ensure that the results contribute in a realistic way to the ongoing debate about the impact of biofuels. Comparative measurements are reported for engine performance as well as the emissions of NO_x, particle number and size distribution, and the concentration of the reactive oxygen species (which provide a measure of the toxicity of emitted particles).

It is shown that the biodiesels used in this study produce lower mean effective pressure, somewhat proportionally with their lower calorific values; however, the molecular structure has been shown to have little impact on the performance of the engine. The peak in-cylinder pressure is lower for the biodiesels that produce a smaller number of emitted particles, compared to fossil diesel, but the concentration of the reactive oxygen species is significantly higher because of oxygen in the fuels.

The differences in the physicochemical properties amongst the biofuels and the fossil diesel significantly affect the engine combustion and emission characteristics. Saturated short chain length fatty acid methyl esters are found to enhance combustion efficiency, reduce NO_x and particle number concentration, but results in high levels of fuel consumption.

KEYWORDS: Biodiesel, fatty acid methyl ester, saturation degree, unsaturation degree, chain length, iodine value, saponification number, NO_x, particle mass concentration, particle size distribution, reactive oxygen species

CITATION: Pham, P., Bodisco, T., Stevanovic, S., Rahman, M. et al., "Engine Performance Characteristics for Biodiesels of Different Degrees of Saturation and Carbon Chain Lengths," *SAE Int. J. Fuels Lubr.* 6(1):2013, doi:10.4271/2013-01-1680.

INTRODUCTION

Widespread introduction of biodiesels into the fuel mix for the transport sector will require a thorough knowledge of its impact on engine performance, with respect to both efficiency and power output, to avoid consumer rejection. Moreover, accurate knowledge of emission output will be critical to the successful implementation of any biofuel. This is particularly relevant as the regulating authorities are

imposing increasingly stringent limits on toxic species, including the number and size distribution of particles [1, 2].

Earlier research of different biodiesel blends have presented an incomplete, and in some cases contradictory, picture about the emission characteristics of biodiesels. A number of reviews discussing the practical use of biodiesels are available on this topic [3,4,5,6]. The production of biofuels is evolving. The variability in the feedstock leads to wide variations in the physical and chemical properties of the

derived fuels and hence their combustion characteristics. This paper studies the effects of the degree of unsaturation and carbon chain length of biodiesels on engine performance and emission output.

A biodiesel is a mixture of fatty acid methyl (or ethyl) esters (FAME) derived from vegetable oils, animal fats or algae, typically by trans-esterification [7,8,9]. FAME is typically written in the format of $R_1\text{-COO-R}_2$ where R_1 and R_2 present the hydrocarbon parts of the carboxylic acid and alcohol, respectively. The alkyl fragment, R_1 , is characterised by its carbon chain length and the number and positions of double bonds (hence the degree of unsaturation). These features strongly affect many physical and chemical properties, such as: viscosity, density, cetane number and calorific value [10,11,12] and hence have a significant impact on the ignition delay and the concentration of combustion products [13,14,15,16,17,18]. Empirical correlations are developed to correlate these relevant properties to the fuel structure using parameters such as iodine values (IV) and saponification number (SN). The iodine value (IV) is the number of grams of iodine consumed per 100 g of fatty acid. It is being used as a measure of unsaturation levels in fatty acid (higher IV indicates a higher degree of unsaturation). The SN is the mass of potassium hydroxide (KOH) required to saponify 1 g of FAME; therefore, SN reflects the carbon chain length (a higher SN implies shorter carbon chain lengths). Some earlier studies of biodiesels [3, 19, 20, 21] reported the effects of varying the IV and SN on the engine performance. However, there are contradictory statements regarding the influence of IV and SN on engine emissions, especially NO_x and particle size distribution.

Lapuerta et al. [3] tested four biodiesels with IV's ranging from 90 to 125 in a 2.2 litre, four-cylinder, turbo-charged direct-injection, compression-ignition engine. They found that increasing the unsaturation degree results in an increase in NO_x and a decrease in particle mass and mean particle diameter. These conclusions are confirmed by Benjumea et al. [19] who also found that NO_x emissions increased with the level of unsaturation. Benjumea et al. [19] also found that an increase in the level of unsaturation leads to a decrease in hydrocarbon (HC) and carbon-monoxide (CO) formation.

Schönborn et al. [20] studied the influences of the FAME molecular structures and found that at constant injection timing an increase in carbon atoms results in a reduction in specific NO_x, with almost no change in specific particle mass concentration, when the number of carbon atoms varied between 12 to 18. However, particle mass was more than doubled when the number of carbon atoms increased from 18 to 22. Another study [21] of the effects of carbon chain lengths showed that an increase in chain length resulted in increases in NO_x, HC, CO, volatile organic fractions and soot. An increase in NO_x emission was also observed with increasing levels of unsaturation. Soot produced from short chain FAME was found to be easier to oxidise.

Wilson et al. [22] examined the soot morphology and nanostructure of several biodiesels, including: canola methyl ester, soy methyl ester, a 50:50 mixture of soy methyl ester and animal fat, and diesel number 2. This study was conducted in a wick-generated open-air laminar diffusion flame using transmission electron microscopy (TEM) and high resolution TEM. The soot samples were collected using a probe which adopted the Brownian thermophoretic technique developed by Dobbin and Megaridis [23]. Their results showed that the primary soot diameters of biodiesels were significantly higher than those of fossil diesel.

An important issue that is not widely understood is the effect of biodiesels on the size distribution of emitted particles and related reactive oxygen species (ROS). A shift in the size distribution to nano-sized particles would be undesirable because of the increased health risk it would impose [4]. Moreover, the new European emission standards (EU6) will regulate the particle size distribution in addition to the particle mass [1, 24].

Experimental results reported to date on particles size distribution are contradictory [3, 4, 20, 21]. Some researchers [3, 4, 20] report that biodiesels favor a shift to smaller particles, while a recent study [21] shows similar distributions to fossil-based diesels. Additionally, oxidative stress caused by the generation of free radicals and related ROS has been proposed as a mechanism for many of the adverse health outcomes associated with exposure to particulate matter (PM). In addition to particle-induced generation of ROS in lung tissue cells, several recent studies [25,26,27] have shown that particles may also contain ROS. As such, they present a direct cause of oxidative stress and related adverse health effects [25, 26].

This paper aims to further the discussion on the influence of biodiesels on engine performance with a specific focus on the effects of chain length and degree of unsaturation. A heavy-duty, multi-cylinder, common-rail, turbo-charged diesel engine was the engine under investigation because it can be considered representative of a practical modern diesel engine. In order to estimate the environmental and health impacts of the implementation of selected biofuels, performance, emission and oxidative potential outputs were reported. It included the measurement of particle number concentration and size distribution, NO_x concentration and ROS concentration.

This study makes a key contribution by reporting new measurements of ROS for a range of fuel blends using a BPEA (bis(phenylethynyl) anthracene-nitroxide) molecular probe technique [27,28,29]. This new profluorescent nitroxide molecular probe (bis(phenylethynyl) anthracene-nitroxide; BPEA) [30], was developed in an entirely novel, rapid and non-cell based assay, for assessing the oxidative potential of particles (i.e. potential of particles to induce oxidative stress). Profluorescent nitroxides (PFN) are very powerful optical sensors, applicable as detectors of radicals and redox active agents. The probe itself is poorly fluorescent; however, upon radical trapping, or redox activity,

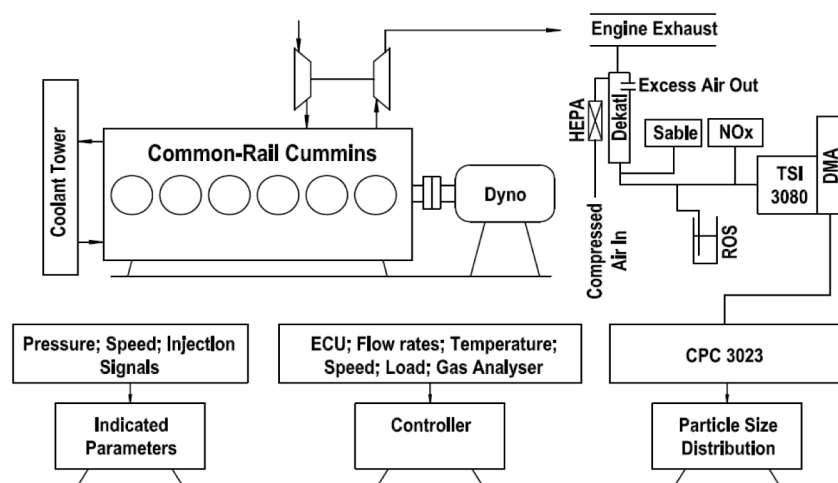


Figure 1. Schematic of the experimental facility

a strong fluorescence is observed. The ROS results reported in this paper result from the application of this technique.

EXPERIMENTAL SETUP

Test Facility

A schematic of the test facility and the specifications of the engine used in this study are shown in Figure 1 and Table 1, respectively. The test bed is a heavy-duty, multi-cylinder, common-rail, turbo-charged diesel engine-typical of those used in buses or medium sized trucks. It is equipped with a hydraulic dynamometer, an engine controller, and a series of exhaust gas analysers to observe, amongst others: NOx, black carbon, particle mass concentration, particle number concentration, and reactive oxygen species. In addition, in-cylinder pressure, crank-angle information and injection profiles were also recorded to further the understanding of fuel air cycle characteristics. The engine controller was developed by Mainline Dynolog Dynamometers [31]. Emission and engine operating data were sampled simultaneously at 1 Hz through the Mainline Dynolog Dynamometers' proprietary software; whereas, the in-cylinder pressure, crank-angle information and injection profile data were sampled at 200 kHz using a Data Translation analogue-to-digital converter (DT9832) and National Instruments LabView.

Particle size distributions are determined using a scanning mobility particle sizer (SMPS-TSI 3080) which fractionates sub-micron particles in an electrostatic classifier (EC) and uses optical detection to analyse particle concentration in the concentration particle counter (CPC-TSI 3025). The exhaust stream is diluted by a Dekati diluter. The EC consists of a bipolar charger (which contains a radioactive Kr-85 generator that produces bipolar ions and applies an equilibrium charge distribution to the aerosol, i.e. the particles are positively charged) and a differential mobility analyser (DMA) (which contains a negatively charged centre rod). The particles extracted from the DMA are supplied to the CPC which

contains a saturator, a condenser, and an optical detector. The particles are vapor-saturated by the saturator, condensed by thermal diffusion and then counted by the detector.

Table 1. Engine specifications (Cummins ISBe220 31)

Number of cylinders	6
Injection type	High-pressure common-rail
Number of valves	4 / cylinder
Bore x stroke [mm]	102 x 120
Swept volume [litre]	5.9
Max. power [kW]	162 (at 2500 rpm)
Max. torque [Nm]	820 (at 1500 rpm)
Compression ratio	17.3:1
Dynamometer type	Hydraulic
Emission standard	Euro III

A piezoelectric pressure transducer (Kistler 6053 CC60) is used to measure the in-cylinder pressure. Nominal injection timing, crank-angle and engine speed signals were also recorded simultaneously with the in-cylinder pressure at 16 bit resolution. In-cylinder data was collected in sets of 60 seconds (600, 750 and 1000 engine cycles correspond with 1200 rpm, 1500 rpm and 2000 rpm, respectively). Data was processed offline by in-house C++ software and then analysed by a 0D thermodynamic model coded in Matlab. Outputs of this process include: peak pressure, peak pressure timing, maximum rate of pressure rise, indicated mean effective pressure, injection timing, and the net heat release rate (NHRR).

The BPEA molecular probe (bis(phenylethynyl) anthracene-nitroxide) described earlier was applied in-situ to assess the oxidative potential of different fuel stocks. Samples were collected by bubbling aerosol through an

Table 2. Fuel properties and compositions

		C810	C1214	C1618	C1875	Commercial Diesel
Hexanoic [wt%]	C6:0	6 max	-	-	-	
Formic [wt%]	C8:0	50-60	-	-	-	
Decanoic [wt%]	C10:0	35-50	1.0 max	-	-	
Lauric [wt%]	C12:0	1.5 max	45-55	-	-	
Miristic [wt%]	C14:0	-	15-20	-	-	
Palmitic [wt%]	C16:0	-	8-15	23-32	4.3	
Stearic [wt%]	C18:0	-	1-5	8	2.2	
Oleic [wt%]	C18:1	-	11-19	53	63.5	
Linoleic [wt%]	C18:2	-	4.0 max	-	18.9	
Linolenic [wt%]	C18:3	-	-	-	9.2	
Heneicosanoic [wt%]	C20:0	-	0.5 max	1.5 max	0.4	
Enoic [wt%]	C20:1	-	-	-	1.1	
Average formulae		$C_{9.5}H_{19.7}O_2$	$C_{14.8}H_{28.3}O_2$	$C_{18.3}H_{35.3}O_2$	$C_{18.7}H_{35.3}O_2$	
O₂ [wt%]		19.29	13.47	11.14	10.96	
Stoichiometric air fuel ratio		11.12	12.05	12.50	12.48	14.5 (for D#2)
Relative density [kg/m³], at 20°C		0.877	0.871	0.873	0.879	0.848
Sulphur [mg/kg]		-	-	-	-	2.5
Iodine number		1.0 max	8	65	105	-
Saponification value		330	233	195	185	-
Boiling point [°C]		190	>150	165.6	>150	-
Acid value		0.9	0.4	0.8	0.4	0.05
Viscosity [m²/s] at 40°C		0.997E-6	2.4E-6	-	4.5E-6	-

impinger containing 20 mL of 4 μ M BPEA solution (using an AR grade dimethylsulphoxide as a solvent) followed by fluorescence measurements with a spectrofluorometer (Ocean Optics). The amount of BPEA reacting with the combustion aerosol was calculated from a standard curve obtained by plotting known concentrations of the methanesulfonamide adduct of BPEA (fluorescent) against the fluorescence intensity at 485 nm [32]. For each setting and particulate source, two samples were taken. The first one was the result of the exposure of the BPEA solution to the particle-free gas phase, which was done by placing a HEPA-filter between an impinger and an aerosol source. A test sample was collected upon exposure to both the particle and the gas phase, demonstrating the effect of the particle-related ROS. Based on the difference in fluorescence signals at 485 nm between the test and HEPA-filtered control sample, the amount of particle-associated ROS emitted for each test sample was calculated and normalised by the particle mass to give ROS concentrations in nmol/mg.

Fuel Selection

Four biodiesels (labeled as: C810, C1214, C1618, and C1875) with different iodine numbers and saponification

values were tested here. These fuels were produced by Procter and Gamble Chemicals [33]. The first two (C810 and C1214) have close iodine numbers (1 and 8) but different saponification values (330 and 233). The last two (C1618 and C1875) have different iodine numbers (65 and 105) but close saponification values (195 and 185). The differences in iodine values and saponification numbers represent differences in the degree of unsaturation and carbon chain length, respectively. Pure biodiesels (B100), pure commercial fossil-based diesel (B0), and blends of 20:80 (B20) and 50:50 (B50) of these biodiesels (with fossil diesel, by volume) were tested at 1200 rpm idling and at 1500 rpm and 2000 rpm at 25%, 50%, 75%, and 100% of full load. Table 2 shows the fuel properties. The oxygen concentration, stoichiometric air fuel ratio, and average molecular formulae, shown in Table 2, are estimated using pure substance compositions (supplied by the manufacturer) and their carbon, hydrogen and oxygen content. It should be noted that key properties, such as surface tension and cetane numbers are unknown for these biodiesels.