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The effect of biodiesel fatty acid composition on combustion and diesel engine exhaust emissions

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HIGHLIGHTS

- ▶ The bulk modulus effect on NO_x trend is more influential for shorter fatty acids.
- ▶ HC, CO and VOF emissions are higher when increasing FAME chain length.
- ▶ Soot formation is mainly influenced by Oxygen content and viscosity of FAME.
- ▶ Soot oxidation characteristics are dependent on the chain length of FAME.

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ABSTRACT

This study investigates the effect of biodiesel chemical structure on diesel engine combustion properties and exhaust emissions in mechanical injection engines, in view of future emissions reduction by tailoring the fatty acid profile or processing of bio-feedstock. To achieve this, the individual fatty acid methyl esters (FAMEs) that make up biodiesel were investigated for combustion and emissions. Research included the effect of FAME molecular structure (saturation degree and chain length). Selected FAME fuels included neat methyl esters and blends with rapeseed oil methyl esters (RME). Several chemical and physical properties of the fatty acids methyl esters were chosen to obtain the most significant properties in terms of PM and NO_x emissions in this type of engines. Each fuel was tested in a single cylinder mechanical direct injection (DI) diesel engine for combustion and exhaust emissions, with particular emphasis upon particulate matter (PM) emissions. Statistical prediction models showed a correlation between exhaust emissions and the most significant fuel properties ranging from 88% to 97%. NO_x emissions were found to increase as chain length (with exception of C18:0) and the degree of unsaturation of fatty acid methyl esters increased. Total hydrocarbons (THCs), carbon monoxide (CO), volatile organic fraction (VOF) and soot emissions increases as the chain length of hydrocarbons increases. Soot produced by short chain length FAME is easier to oxidise than soot from long chain FAME. The recommendation is that shorter chain saturated FAME fuels would be preferable in a combined emissions context.

1. Introduction

Biodiesel is a mixture of mono-alkyl esters of vegetable oils or animal fats [1]. Methyl esters can be produced by transesterifying the parent oil or fat in order to achieve viscosity and flow properties close to that of petrodiesel. The fatty acid profile of biodiesel is dependent on the parent oil or fat. The most common fatty esters contained in biodiesel are derived from palmitic (hexadecanoic) acid, stearic (octadecanoic) acid, oleic (octadecenoic) acid, linoleic (octadecadienoic) acid and linolenic (octadecatrienoic) acid. Conventional feedstocks for biodiesel production include rapeseed, soybean, sunflower, palm, and peanut oils. Some tropical oils, such as, coconut oil, additionally contain significant amounts of shorter

Abbreviations: AFT, adiabatic flame temperature; ANOVA, analysis of variance; BM (β), isentropic bulk modulus; c, speed of sound; CAD, crank angle degree; CN, cetane number; CO, carbon monoxide; CO_2, carbon dioxide; COV, coefficient of variation; ELPI, electronic low pressure impactor; EGR, exhaust gas recirculation; FAME, fatty acid methyl ester; FBP, final boiling point; FID, flame ionisation detector; GC, gas chromatograph; HC, hydrocarbon; HCs, hydrocarbons; HCV, high calorific value; IBP, initial boiling point; IMEP, indicated mean effective pressure; LC, length of chain; LCV, low calorific value; NDIR, non-dispersive infrared; NO_x, nitrogen oxides; O_2, oxygen; PM, particulate matter; R^2, coefficient of determination; RME, rapeseed methyl ester; ROHR, rate of heat release; SMPS, scanning mobility particle sizer; SOC, start of combustion; SOF, soluble organic fraction; TDC, top dead centre; TGA, thermogravimetric analysis; THC, total hydrocarbons; UD, unsaturation degree; ULSD, ultra low sulphur diesel; VOC, volatile organic compounds; VOF, volatile organic fraction; VOM, volatile organic material; ρ, density.

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chain acids, such as caprate (decanoic) and lauric (dodecanoic) acids [2].

Many authors have found that particulate matter (PM) [3,4], hydrocarbons (HCs) [5] and carbon monoxide (CO) [6,7] are reduced through the use of biodiesel. However, NO_x emissions are increased [7–9]. The reduction of NO_x exhaust emissions is one of the most important technical challenges facing biodiesel, especially in light of the increasingly stringent exhaust emissions regulations affecting diesel engines [10]. Biodiesel emissions can be improved by blending [11], using additives [12] or indeed modifying the fatty ester composition of biodiesel [13].

Advances in molecular biology research [14] make it possible to improve the fatty acid profile of vegetable oils to enhance the fuel properties of biodiesel. Genetic modification of fatty acid composition could offer a method to address fuel property issues simultaneously. For example, the presence of some esters (e.g., methyl caprate and methyl oleate) could be increased or the content of polyunsaturated methyl ester could be reduced. Recently, some authors [15] reproduced a complete genetic bacteria system by chemical synthesis, starting with only the digitized DNA sequence. Synthetic genomic discoveries open the door to many applications in the bioenergetics field, one of these is the production of oilseed crops able to produce a specific fatty acid profile.

Various studies on chemical and physical properties of biodiesel have suggested that biodiesel with a high level of methyl oleate (or monounsaturated fatty acid) may have excellent characteristics in regard to ignition quality, fuel stability, flow properties at low temperature, and iodine number (according to European biodiesel standard EN 14214) [2,16]. Recently, some authors have found esters of saturated medium chain acids to be suitable, most especially esters of decanoic (capric) acid [2,17]. This is because they show reasonable cold flow properties and are an alternative to the long-chain saturated fatty acid esters with high melting points, whilst possessing excellent oxidative stability due to the absence of double bounds. Lastly, they are also preferred to polyunsaturated fatty acids (i.e. C18:3), that have a negative effect on the auto-oxidation of biodiesel [18].

The influence of the chemical structure of fatty acids composition on biodiesel physical and chemical properties has been demonstrated in several studies [2,13,16,19]. Moreover, some studies show a direct correlation between the chemical structure of fatty acids and exhaust emissions [10,20,21]. It has been found that NO_x exhaust emissions increased with the reduction of the mean carbon chain length and the increase of the unsaturation degree [21]. The influence on the formation of NO_x appears to be exerted primarily by the effect which the molecular structure had on the auto-ignition delay occurring after the fuel was injected into the combustion chamber (cetane number, CN), and to a lesser extent by the flame temperature at which the fuel burnt [21]. Reductions in total hydrocarbons (THCs) and CO emissions with an increase of biodiesel chain length has been reported [10,20], but no clear conclusion concerning saturation level has been reached.

However, the effect that the chemical structure of biodiesel has on the formation of PM remains unclear [10,22]. Some authors state [12,20,23] that the main factor affecting PM formation is the oxygen content in the fuel though, there is argument to include many factors such as, CN, viscosity, aromatic content, bulk modulus, C/H ratio, final distillation temperature, sulphur content, (all fuel dependent) and the engine and injection system type. Moreover, to the best of our knowledge, the correlation of fatty acid composition and size distribution of particles are not cleared yet. Recent studies have shown that oxygenated fuels produce evidently dissimilar particulate, with a shift towards a smaller mean particle size [12,24]. Krahl et al. [25] comparing the particle size distribution of blends of FAME with different fatty acids composition observed some differences, but they could not explain the tendency obtained.

The aim of this work is to determine the effect of the ester molecular structure (number of double bonds and chain length) on combustion and emissions properties, in order to facilitate recommendations for the design of the chemical structure of future biodiesel raw materials. In this work, seven fatty acid methyl esters from caprate, myristate, laurate, palmitate, stearate, technical grade oleate and linoleate were selected for exhaust emissions testing and were used neat and/or blended with RME. These fatty acids were tested for combustion and emissions in an unmodified DI diesel engine with particular emphasis upon PM emissions.

2. Materials and methods

2.1. Apparatus

Experiments were conducted using a Lister-Petter TR1 single cylinder, pump-line-nozzle, mechanical direct injection diesel engine. One single injection was used and injection timing was maintained constant. The fuel injector is located near the combustion chamber centre and has an opening pressure of 180 bar. The combustion chamber is a bowl-in-piston design. Table 1 shows a detailed engine specification. The single cylinder diesel engine test rig consists of a thyristor-controlled DC motor-generator machine dynamometer coupled to a load cell and is used to load and motor the engine.

In-cylinder pressure traces were acquired by a Kistler 6125B quartz type pressure transducer, with a Kistler 5011 charge amplifier at crank shaft positions, determined by a 360-ppr incremental shaft encoder, with data recorded by data acquisition board National Instruments PCI-MIO-16E-4, installed in a PC. In-house developed LabVIEW based software was used to obtain pressure data and analyse combustion parameters, e.g. coefficient of variation (COV) of indicated mean effective pressure (IMEP), peak pressure, indicated power and heat release.

The exhaust gas recirculation (EGR) flow was controlled manually by a valve. The EGR level was determined volumetrically as the percentage reduction in volume flow rate of air at a fixed engine operating point. A Horiba Mexa 7100DEGR analyzer was employed to measure the concentrations of NO_x, CO, CO_2, O_2 and THC. This equipment measures NO_x ($NO + NO_2$) by chemiluminescence, CO and CO_2 are measured using non-dispersive infrared (NDIR), O_2 by an electrochemical method and hydrocarbons (THCs) by flame ionization detection (FID).

A TSI SMPS 3080 particle number and size classifier with thermodiluter was employed to measure the particle size distribution of PM emitted from the engine. The dilution ratio was 1 part exhaust to 32 air. Once the particle number distribution is obtained, it can be transformed into volume and later to a particle mass distribution using an agglomerate density function which decreases as agglomerate size increases [26].

Particulate matter (PM) was collected using an in-house developed Venturi nozzle diluter (8:1) located at the same position in the exhaust as all the analysers utilized. PM was collected on

Table 1
Engine specifications.

Engine	
Injector	3 hole Ø 0.25 mm
Bore	98.4 mm
Stroke	101.6 mm
Displacement volume	773 cm^3
Maximum torque	39.2 Nm @ 1800 rpm
Maximum power	8.6 kW @ 2500 rpm
Compression ratio	15.5:1
Con-rod length	165.0 mm