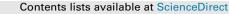
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# Factors affecting biodiesel engine performance and exhaust emissions – Part I: Review

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#### ABSTRACT

Effects of variation in biodiesel fuel properties on engine performance are not completely understood and there is a need for further research. A review of literature studies on biodiesel engine performance and emissions is presented here, summarising known effects and highlighting aspects in need of further study. In particular, it is evident few studies have reported on the effects of biodiesel oxidation, and antioxidant additives. It is well known that physical properties of biodiesel such as the bulk modulus and viscosity alter the injected fuel-spray characteristics. Biodiesel's greater density and oxygenated structure results in proportionally lower energy content. Unsaturation level affects Cetane number and combustion characteristics. Maximum engine power usually decreases according to the lower volumetric energy content of biodiesel, and fuel consumption is expected to increase around 14%. Impacts on emissions are difficult to conclude generally due to contrasting reports. However, dominant emissions trends are usually an increase in oxides of nitrogen, and decreases in carbon monoxide, particulate matter, unburned hydrocarbons and aromatics. Changes in emissions of carbonyl compounds are less certain. The effect of alcohol type used in biodiesel production is not clear, neither is the effect of biodiesel oxidation and antioxidant additives.

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#### 1. Introduction

Increasing awareness of the depletion of fossil fuel resources as well as their negative environmental impacts has triggered interest in the potential benefits of 'biofuels' such as biodiesel, which is an alternative fuel for diesel engines. Biodiesel is a drop-in replacement for petro-diesel that is biodegradable, less toxic and can reduce harmful tailpipe combustion emissions (CO<sub>2</sub>, CO, UHC (unburned hydrocarbons) and PM) relative to petro-diesel [3]. Biodiesel is miscible with petro-diesel, compatible with fuel delivery infrastructure, has high flashpoint for safer handling, and can be used in standard diesel engines requiring no engine modification. It is an oxygenated, renewable fuel, that compared to petro-diesel usually has higher Cetane number, and contains no sulphur or aromatic compounds [4]. Biodiesel also offers improved lubricity over certain low-sulphur petro-diesels [5] and thus can help reduce wear of engine components [6]. Running diesel engine equipment

http://dx.doi.org/10.1016/j.energy.2014.04.015 0360-5442/© 2014 Elsevier Ltd. All rights reserved. on biodiesel can be beneficial in terms of environmental impact and energy security. In the United Kingdom, the Renewable Transport Fuels Obligation (RTFO) currently mandates an aggregate 5% by volume EN 14214 quality-grade biodiesel to be blended with petrodiesel sold from UK forecourts. In Europe, biodiesel should meet the fuel quality standard known as EN 14214 [7] to be approved for use in diesel engines; limits are imposed on a range of important fuel properties, including: purity, combustion properties and fuel stability.

Biodiesel is produced mainly from plant-seed oils: rapeseed in Europe, soybean in USA and also more generally from used cooking oil (UCO), though can be derived from a wide range of other seed oils, animal fats and even certain lipid-rich algal species. The main molecular component of oils and fats are triglycerides, also known as triacylglycerols (TAG). Biodiesel is conventionally made via the alkaline-base catalysed chemical reaction known as transesterification, which converts TAG and alcohol into fatty acid alkyl esters (FAAE), forming glycerol as co-product. Alkoxide anions (R'O<sup>-</sup>) generated by the base-catalyst in mixture with the alcohol drives the reaction, as discussed by literature authors [8–10]. Methanol (CH<sub>3</sub>OH) is typically used, yielding fatty acid methyl esters (FAME).



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The transesterification reaction is a sequence of three consecutive and reversible reactions in which di-acylgylcerols (DG) and mono-acylglycerols (MG) are formed as intermediates, before finally liberating glycerol. The reaction proceeds stepwise via DG and MG, with a fatty acid alkyl ester being formed in each step [11.12].

In practice, the starting oil/fat is heated and vigorously mixed with a solution of base-catalyst and methanol usually for around 1 h, under atmosphere and below methanol boiling point (65 °C). The product is allowed to settle before it is purified by decanting glycerol and final washing [13]. The transesterification reaction must be sufficiently complete and the FAME purified in order to meet fuel quality standards such as EN 14214.

The main purpose of transesterification is primarily to reduce viscosity of TAG to a value much closer to that of conventional petro-diesel. Without converting TAG to FAEE (Fatty acid ethyl ester), the high viscosity of TAG results in poor atomization upon injection into the combustion chamber and leads to operational problems in diesel engines, such as deposit formation on engine parts, and eventual engine failure [14]. High viscosity and low volatility of TAG causes severe engine deposits, injector coking, and piston ring sticking [4]. Though some engines can be designed or modified to use un-transesterified TAG, the vast majority of engines require lower-viscosity fuel [6].

A review of literature on the effect of biodiesel fuel on engine performance (power, fuel consumption) and emissions, including: regulated emissions such as nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), particulate matter (PM), hydrocarbons (HC), and other non-regulated emissions, such as poly-aromatic hydrocarbons (PAHs), aldehydes, and acrolein. Dominant trends in these parameters are reported in most cases: a slight power loss, an increase in fuel consumption, an increase in emissions of NO<sub>x</sub> and carbonyl compounds, and reduction in emissions of PM, HC, aromatic compounds and CO, when biodiesel is run in un-modified conventional diesel engines. However, contrasting trends are also evident in some cases. Possible reasons for variation in trends reported include the different engine technologies, measurement techniques, operating conditions/drive cycles, and fuel with varying feedstocks and fuel qualities employed amongst different studies.

#### 1.1. Impacts of biodiesel fuel properties

Experimental study of biodiesel combustion carried out by Rao Pulagala et al. [1] investigated the causes of changes in combustion, and emission characteristics when running biodiesel; examining the effects of fuel properties on injection. Properties of petro-diesel (see Table 1) were compared with biodiesels: Rice bran oil methyl ester (RBOME) and sesame seed oil methyl ester (SSOME). Fuel properties measured by investigators Bannister et al. [2] for rapeseed methyl ester (RME) and ultra low-sulphur petro-diesel are included in Table 1 for comparison. Elemental analysis showed petro-diesel contained  $\sim 0\%$  oxygen, compared to  $\sim 10\%$  oxygen for biodiesel. The presence of oxygen reduced the calorific value of the biodiesels approximately 10% relative to petro-diesel. Bulk modulus of biodiesel was greater than petro-diesel, indicating biodiesel was less compressible. Biodiesel density was  $\sim 6\%$  greater, and viscosity was approximately twice that of petro-diesel. The CN of biodiesels measured [1] met the lower limit (>51) defined by respective European fuel standards (EN 590, EN 14214). Whereas the CN of RME tested by Bannister et al. [2] was less than 51 due to unusually high levels of unsaturated methyl linolenate. As discussed later, for example by Lapuerta et al. [15], it is well known that alkyl ester CN increases with fatty acid chain length and decreases with unsaturation, so that biodiesel CN depends on the biodiesel fatty acid profile.

#### Table 1

Comparison of biodiesel and petro-diesel fuel properties obtained from the literature.

Property	Units	Reference				
		Rao Pulagala et al. [1]			Bannister et al. [2]	
		Petro-diesel	SSOME	RBOME	Petro-diesel	RME
Density @15 °C	kg/m <sup>3</sup>	820	870	870	833	883
Kinematic viscosity @40 °C	mm <sup>2</sup> /s	2.2	3.9	4.5	2.75	4.56
Flashpoint Cetane number	°C	66 48	158 52	153 57	65 52.8	182 49.5
Cold filter plugging point	°C	-	-	_	-18	-20
Net calorific value	MJ/kg	42.5	37.6	38.6	42.6	40.0
Sulphur content	mg/kg	0.3	0.0	0.0	7.0	1.8
Carbon content	%m/m	86.3	77.3	77.8	86.2	77.1
Hydrogen content	%m/m	12.5	11.8	11.8	13.8	12.2
Oxygen	%m/m	0.3	10.0	9.4	0.0	10.7
Acid value Bulk modulus	mg KOH/g MPa	— 1475	_ 1800	_ 1800	0.2	0.18 -

Similar fuel property data (Table 2) was reported by Hoekman et al. [16] for 12 common biodiesel FAME types: Canola, palm, rapeseed, soy, corn, safflower, sunflower, yellow grease (used cooking oil), tallow, camelina, jatropha, and coconut. All CN values for these biodiesels were >51, except for camelina which contained very high levels of methyl linolenate. The CN of the more unsaturated FAME types produced from safflower, soybean, and sunflower oil feedstocks were marginally higher than 51. The highest CN values (>58) were observed for FAMEs containing more saturated fatty acids: palm, coconut, and tallow. Biodiesel CN therefore varies considerably according to feedstock type and can be significantly higher than CN values reported for petro-diesel (see Table 1). Further study appears warranted, that would compare biodiesel fuel properties measured for a wide range of different feedstocks (obtained by the same operator using the same equipment).

Engine testing of RBOME, SSOME, and petro-diesel fuels by Rao Pulagala et al. [1] was performed on a single-cylinder diesel engine with a cam-driven, pump-line-nozzle fuel injection system. The 'column of fuel' present between the pump plunger and the injector was described to behave like a stiff spring, where injector pump pressure pulses propagated through the 'column of fuel' to develop pressure at the fuel injection nozzle and open the injector needle valve. Pressure waves propagate more rapidly through fuels which possess higher bulk modulus (are less compressible), so that in pump-line-nozzle fuel injection systems, the needle valve lifts sooner and injection commences earlier with biodiesel fuel of higher bulk modulus.

Experiments performed by Rao Pulagala et al. [1] measured peak combustion pressure and the crank angle position of peak pressure, for the biodiesels compared to petro-diesel. Results showed peak pressures for biodiesels were higher and occurred closer to TDC. This was attributed to the higher bulk modulus of biodiesel, which caused earlier needle valve lift and advanced injection. Interestingly, increasing the fuel temperature reduced biodiesel bulk modulus which delayed valve lift, and peak pressure was thus reduced and occurred further from TDC. Whether or not biodiesel bulk modulus is dependent on feedstock type and fatty acid

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