



The influence of straight vegetable oil fatty acid composition on compression ignition combustion and emissions



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HIGHLIGHTS

- Combustion and emissions of 7 vegetable oils (SVO) including one from micro-algae.
- Tested in a common-rail direct injection compression ignition engine.
- Strong correlation of SVO mean fatty acid degree of saturation with ignition delay.
- Heat release rates increase with oil viscosity due to fuel impingement.
- Particulate emissions are affected by fatty acid molecular structure and viscosity.

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ABSTRACT

This paper presents experimental studies carried out on a modern direct injection compression ignition engine supplied with a range of straight vegetable oils to investigate the effect of oil fatty acid composition on combustion and emissions. Seven oils, those of corn, groundnut, palm, rapeseed, soybean, sunflower and the micro-algae species *Chlorella protothecoides* were tested, with all of the fuels heated to 60 °C, at constant injection timing and constant ignition timing at a constant engine speed of 1200 rpm. All of the vegetable oils exhibited a duration of ignition delay within ± 0.6 CAD of that displayed by a reference fossil diesel, but displayed much reduced rates of peak heat release rate. The duration of ignition delay was found to increase with an increasing carbon to hydrogen ratio of the vegetable oils, implicating the fatty acid alkyl chain as the primary driver of low temperature reactivity. Peak heat release rates decreased with decreasing vegetable oil viscosity, suggesting a significant degree of fuel cylinder wall and piston bowl impingement. At both injection timings, emissions of NO_x were lower for all of the vegetable oils relative to the reference fossil diesel, while those of CO, THC and particulate matter were higher and sensitive to the injection timing.

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1. Introduction

Vegetable oils were amongst the first widely considered alternatives to liquid fossil fuels, and the products of transesterification of such oils with alcohols are now widely used as biodiesel. However, while the use of biodiesel does reduce tailpipe emissions of fossil bound carbon, which as carbon dioxide contribute to anthropogenic global warming, there are increasing concerns as to the sustainability of such biodiesels when considering the entirety of the fuel lifecycle [1]. Therefore, given that the conversion of vegetable oils to biodiesel requires an additional input of energy and materials (usually an alcohol in the form of fossil-derived metha-

nol [2]), it is useful to re-examine the use of non-transesterified straight vegetable oils for the displacement of fossil fuels in the context of modern combustion technology.

In the early 1980s, concern as to the security of supply of fossil fuels saw the use of vegetable oils as a replacement investigated, especially in the context of agricultural usage [3,4]. Vegetable oils are predominately made up of triglycerides, molecules which consist of three fatty acids joined by a glycerol group. While the structure of the fatty acids that make up the triglycerides, and the level of each triglyceride species present, varies from oil to oil, it is the long alkyl chain present in the fatty acids that make the oils suitable for compression ignition combustion. However, the use of vegetable oils was found to compromise the durability of compression ignition engines, in particular by increased injector nozzle coking, piston ring sticking and dilution of the engine lubrication oil [3,5].

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Nomenclature

NO _x	nitrous oxides	SOI	start of injection
CO ₂	carbon dioxide	BTDC	before top-dead-centre
CO	carbon monoxide	TDC	top-dead-centre
THC	total hydrocarbons	SOC	start of combustion
CAD	crank angle degree	IMEP	indicated mean effective pressure
PID	proportional integral derivative	PPM	parts per million
DAQ	data acquisition	FAME	fatty acid methyl ester
O ₂	oxygen	SVO	straight vegetable oil

Ryan et al. [5] studied the combustion of several vegetable oils, at various stages of refinement, in a heated and pressurised constant volume chamber and also in direct and indirect compression ignition engines. In this study, all of the oils were heated from 40 °C to 145 °C so as to reduce the viscosity of oils to a level similar to that of a reference fossil diesel. It was expected by Ryan et al. that reducing fuel viscosity would increase fuel atomization on injection, and also decrease the penetration rate of the spray (rate of spray tip travel from the injector nozzle) with a concurrent increase in the cone angle of the spray. However, heating of the oils, while reducing viscosity, actually increased the penetration rate and decreased the cone angle. In combustion tests, the direct injection engine was found to both suffer more of the durability issues relative to the indirect injection engine and a greater sensitivity to the composition of the vegetable oils.

Transesterification of vegetable oils to fatty acid esters was found to diminish many of the durability issues encountered in the use of vegetable oils [6,7]. Nevertheless, use of straight vegetable oils, neat and blended with fossil diesel, has persisted [8–17]. There have been several reviews [18–21] on the use of vegetable oils, which have repeatedly highlighted the dependence of engine durability, combustion phasing and emissions production on fuel temperature and the subsequent physical properties of the vegetable oil.

Recently, there have been several studies which have sought to characterise the effect of heating on straight vegetable oils [22]. Franco and Nguyen [23] measured the dynamic viscosity of six vegetable oils, and found that at all temperatures (20–80 °C) the viscosity decreased with a decreasing degree of saturation of the fatty acid alkyl chains. The same observation was made by Santos et al. [24] who found a better correlation between viscosity and the level of alkyl chains containing more than two double bonds (polyunsaturates) than those containing only one double bond.

Deshmukh et al. [25] undertook optical spray characterisation of two vegetable oils of differing viscosity (pongamia and jatropha), utilising a single hole solenoid valve injector at an injection pressure of 1600 bar. For the spray characterisation, both oils were heated to 60 °C, and at a lower temperature of 40 °C the pongamia and jatropha oils exhibited dynamic viscosities of 37 mPa s and 30 mPa s respectively. Measurement of the injection delay was made (defined as the interval between commencement of injector actuating signal and the first appearance of fuel at the injector tip) and found to be of longer duration for the oil of higher viscosity (pongamia). Furthermore, the more viscous oil exhibited greater injection to injection variability in the duration of injection delay. This was attributed to the greater degree of resistance presented by the more viscous oil to the opening of the injector needle. Pongamia oil also exhibited a lower penetration rate relative to the less viscous jatropha oil, and it was suggested that the higher viscosity of the former reduced the momentum of the spray during injection.

Pinzi et al. [26] investigated the effect of vegetable oil fatty acid composition on the physical properties of the fatty acid methyl esters of the same vegetable oil. They found that the lower heating

value, cetane number and kinematic viscosity of the fatty acid esters increased with the carbon chain length of the vegetable oil fatty acid alkyl chain and decreased with decreasing saturation. While the alkyl carbon chain length influenced most the lower heating value of the fatty acid esters, cetane number was most affected by the degree of saturation. Mehta and Anand [27] investigated the effect of fatty acid composition on vegetable oil lower heating value, and found a similar influence of alkyl chain carbon length and degree of saturation on lower heating value, with an increase in both properties raising the lower heating value of the vegetable oil.

This paper presents results of combustion experiments with six edible straight vegetable oils, and one non-edible oil from micro-algae, as un-blended fuels in a single-cylinder direct injection compression ignition engine, undertaken so as to develop scientific knowledge useful for the rapid screening of potential vegetable oil fuels. Combustion characteristics and emission levels are compared to a reference fossil diesel and the influence of the vegetable oil chemical and physical properties on these characteristics investigated.

2. Experimental methods

2.1. Apparatus

A modern direct injection diesel engine, converted to run as a single cylinder research engine, was utilised for all of the combustion experiments described in this work. As the straight vegetable oils under study possessed viscosities much higher than fossil diesel, and in the case of the oil from micro-algae available in very limited quantity, use was made of a novel low volume fuel system for high pressure direct injection (sample fuel volumes of 100–250 mL at injection pressures up to 1600 bar). This engine test facility, and the experimental methodology employed, has been described in detail by the author in previous studies [28,29]. For all experiments, the low volume fuel system and sample fuel lines were held at a constant temperature of 60 ± 2.5 °C, and the engine was normally aspirated with air at atmospheric temperature and pressure throughout. Table 1 gives further specifications of the engine, while Fig. 1 displays the operating principles of the low volume fuel system in schematic form.

In addition to measurement of the in-cylinder gas pressure, for all tests the composition of the engine exhaust gas was determined with an automotive gas analyser system (Horiba MEXA9100 HEGR) and a fast particulate spectrometer (Cambustion DMS 500), conducted at the sampling conditions described previously by the author [28,29].

2.2. Fuels investigated

Seven straight vegetable oils were tested so as to investigate the effect of natural oil fatty acid composition on compression ignition

Table 1
Engine specification.

Engine head model	Ford Duratorq
Engine bottom end model	Ricardo Hydra
Number of cylinders	1
Cylinder bore	86 mm
Crankshaft stroke	86 mm
Swept volume	499.56 cc
Compression ratio	15.8:1
Maximum cylinder pressure	150 bar
Peak motoring pressure at test conditions	36 bar
Piston design	Central ω – bowl in piston
Oil temperature	80 \pm 2.5 $^{\circ}$ C
Water temperature	80 \pm 2.5 $^{\circ}$ C
Fuel injection pump	Single – cam radial – piston pump (BOSCH CP3)
High pressure fuel rail	Solenoid controlled, max. 1600 bar (BOSCH CRS2)
Injectors	6 – hole solenoid controlled (DELPHI DFI 1.3)
Electronic fuel injection system	1 μ s resolution (EMTRONIX EC-GEN 500)
Shaft encoder	0.2 CAD resolution

combustion and exhaust emissions: sunflower, soya, rapeseed, palm, groundnut, corn and algal. All of the vegetable oils were obtained as commercially available edible oils for domestic use, except the algal oil which was produced and harvested from the micro-algae species *Chlorella protothecoides*.

A reference fossil diesel with zero FAME content was also tested. For each vegetable oil, the range of fatty acid composition reported in literature, and precisely measured values of the carbon to hydrogen ratio, are presented in Table 2. The fatty acid molecular structures are shown in Table 3, and the physical properties of each fuel are given in Table 4.

2.3. Experimental conditions

The engine tests of each vegetable oil and the reference fossil diesel were conducted at constant fuel injection timing and repeated at constant start of ignition timing.

At constant injection timing, a constant start of injection (SOI) of 7.5 CAD BTDC was used, where SOI was taken to be the time at which the injector actuating signal commenced, while the start of combustion (SOC) for each fuel varied in accordance with the

duration of ignition delay exhibited by the fuel. For constant ignition timing, the SOC (defined in CAD as the time of minimum cumulative heat release after SOI and prior to that of peak heat release rate) always occurred at TDC by variation of the SOI, as determined by the observed ignition delay.

For all engine tests, fuels were first heated in a PID controlled water bath held at 60 $^{\circ}$ C before filling of the low volume fuel system, which was held at a constant temperature of 60 \pm 2.5 $^{\circ}$ C throughout the subsequent experiment. An elevated fuel temperature of 60 $^{\circ}$ C was used as preliminary experiments with un-heated oils resulted in extremely unstable combustion, unsuitable for making relative assessments of the various oils. The low volume fuel system and injector were flushed with the reference fossil diesel immediately after each vegetable oil test via the bypass shown in Fig. 1.

All tests were conducted at low load conditions at an engine speed of 1200 rpm and a fuel injection pressure of 450 bar, and to maintain a constant engine IMEP of 4.00 bar in the case of every fuel, the injection duration was varied accordingly between 602 μ s and 764 μ s. The engine tests were conducted over four consecutive days of testing, with each day bracketed by tests of the reference fossil diesel, and the running order of the vegetable oils varied from day to day. Table 5 shows the engine and test operating conditions for each combustion experiment with all in-cylinder pressure data presented the average of 100 consecutive combustion cycles.

3. Results and discussion

Fig. 2 shows the in-cylinder pressures and apparent net heat release rates of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing. Apparent at both timing conditions, is the significantly higher peak in-cylinder pressures and heat release rate of the reference fossil diesel relative to the oils (Fig. 2). Furthermore, it can be seen that in the case of the reference fossil diesel the majority of heat release occurs during premixed combustion, whereas all of the oils show a more pronounced period of diffusion controlled combustion (Fig. 2). Also apparent in Fig. 2, is a variation between all fuels in the in-cylinder pressure prior to SOC. The offset between the diesel start and diesel end tests suggests that this variation in in-cylinder pressure is not attributable to fuel vaporisation after SOI, and an offset of this

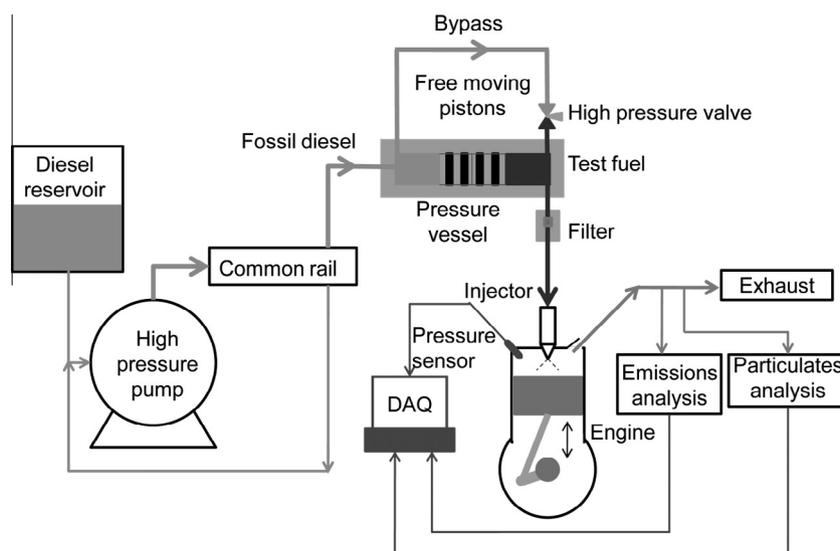


Fig. 1. Schematic showing operation of the low volume fuel system.

Table 2
Vegetable oil fatty acid composition [1].

Source oil	Fatty acid								Molar carbon to hydrogen ratio (C:H) ^a
	C8:0–C14:0	C16:0 (palmitic)	C16:1 (palmitoleic)	C18:0 (stearic)	C18:1 (oleic)	C18:2 (linoleic)	C18:3 (linolenic)	Other	
Algal ^b	0	51.0	0	2.0	39.0	7.0	0	1.0	0.516
Corn	0–0.6	8.6–16.5	0–0.4	1–3.3	20–42.2	39.4–62.5	0.5–1.5	0.5–2.1	0.561
Groundnut	0	6–14	0	2–6	36.4–67.1	13–43	0	0	0.544
Palm	0–2	40–47	0–0.6	3–6	36–44	6–12	0–0.5	0–0.1	0.535
Rapeseed	0–0.2	3.3–6.0	0–3.0	4–6	52–65	18–25	10–11	0–7.4	0.555
Soybean	0–0.2	8–13.3	8–13.3	3–5	18–26	49–57	6–9	0.3–2.4	0.554
Sunflower	0–0.3	5.6–7.6	0–0.3	3–6	14–40	48–74	0–0.2	0–2.4	0.558

^a Experimentally determined data.

Table 3
Fatty acid molecular structure.

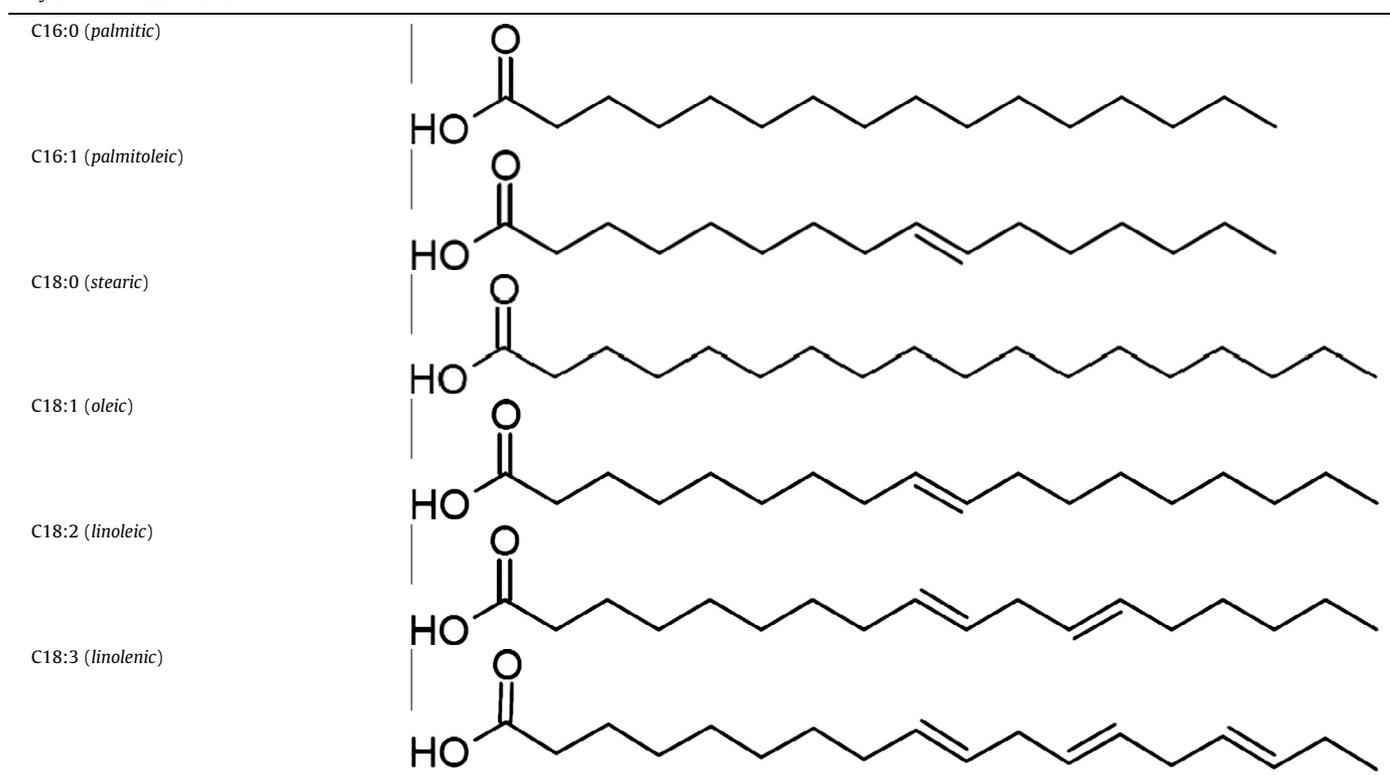


Table 4
Fuel physical properties.

	Flash point (°C)	Cetane number	Density at 20 °C (kg m ⁻³)	Dynamic viscosity at 19.7 °C (mPa s)	Dynamic viscosity at 59.7 °C (mPa s)	Lower heating value (MJ kg ⁻¹)	Surface tension (mN m ⁻¹) at 60 °C
Reference fossil diesel	66.5 ^c	51.7	834.5 ^a	3.41	1.72	43.14 ^b	–
Algal	220.0	–	912.0 ^d	79.87	18.70	35.8	21.04 ^e
Corn	277.0 [2]	37.6 [2]	916.7 [3]	66.57	16.70	39.50 [2]	30 [4]
Groundnut	271.0 [2]	41.8 [2]	902.6 [2]	86.70	19.87	39.80 [2]	–
Palm	330.0 [5]	42.0 [6]	910.0	87.67	19.40	36.54 [6]	30.7 [4]
Rapeseed	246.0 [2]	37.6 [2]	914.5 [3]	73.97	18.00	39.70 [2]	28 [4]
Soybean	254.0 [2]	37.9 [2]	918.5 [3]	71.90	17.60	39.60 [2]	30.7 [4]
Sunflower	274.0 [2]	37.1 [2]	916.9 [3]	69.50	17.20	39.60 [2]	30.5 [4]

^a Experimental data obtained according to ASTM D4052 at 15 °C.

^b Calculated from experimental data obtained by the IP12 method [7].

^c Experimental data obtained according to EN ISO 2719.

^d Data at 25 °C. Values of viscosity were measured at temperatures of 19.7 °C and 59.7 °C using a stand-alone rheometer (Brookfield LVDV – III + U).

^e Data obtained at 26.8 °C.

Table 5
Engine and test operating conditions.

Fuel	Engine speed (rpm)	Fuel injection pressure (bar)	IMEP (bar)	Constant injection timing (SOI at 7.5 CAD BTDC)						Constant ignition timing (SOC at TDC)					
				Ignition delay (CAD)		Injection duration (μs)		Indicated thermal efficiency (%)		Ignition delay (CAD)		Injection duration (μs)		Indicated thermal efficiency (%)	
				Mean	1δ	Mean	1δ	Mean	1δ	Mean	1δ	Mean	1δ	Mean	1δ
Reference fossil diesel	1200	450	4	7.2	0.2	602	5	42.97	0.40	7.1	0.1	604	4	42.81	0.43
Algal	1200	450	4	6.9	–	737	–	41.10	0.00	6.8	–	743	–	40.21	–
Corn	1200	450	4	7.7	–	752	–	37.07	0.00	7.5	–	754	–	36.88	–
Groundnut	1200	450	4	7.1	–	746	–	36.50	0.00	7.1	–	743	–	36.28	–
Palm	1200	450	4	6.9	–	747	–	39.94	0.00	6.8	–	747	–	39.44	–
Rapeseed	1200	450	4	7.7	0.0	764	12	36.87	0.30	7.7	0.1	759	8	36.59	0.26
Soybean	1200	450	4	7.7	0.4	760	13	37.21	0.43	7.6	0.3	761	14	36.92	0.15
Sunflower	1200	450	4	7.5	0.4	756	20	37.27	0.45	7.6	0.5	750	18	36.53	0.35

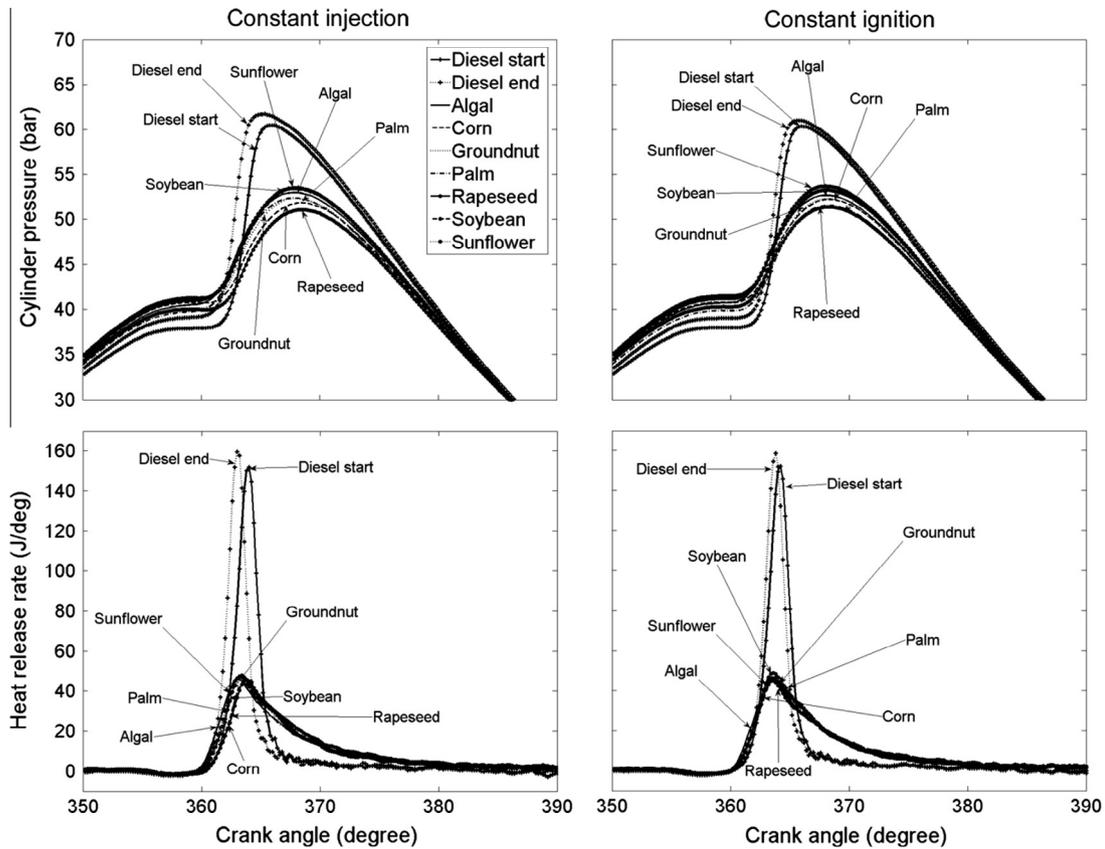


Fig. 2. In-cylinder pressures and apparent net heat release rates of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing.

significance has not been observed in previous tests with different fuels using the same experimental equipment [29,30]. Therefore, it is hypothesised that injection and combustion of the oils resulted in a change to the effective compression ratio of the engine, possibly by reduction of blowby due to fuel wall-wetting and formation of fuel deposits on the piston rings, as has been observed in other engine tests with straight vegetable oils [3,5]. The data shown in Fig. 2 is from a single test of each fuel (and not the mean of repeat experiments as present in all subsequent figures), and for this data set the order of testing was as follows: diesel start, palm, rapeseed, groundnut, algal, corn, sunflower, soya and diesel end. Fig. 2 does therefore potentially indicate a cumulative effect of the vegetable

oils on the suggested reduction of blowby (rapeseed oil, tested early on, and soybean oil, tested last, showing one of the lowest and highest increases in in-cylinder pressure prior to SOC respectively). However, relative to the in-cylinder pressure prior to SOC observed in the previous vegetable oil test, a decrease in the in-cylinder pressure prior to SOC was noted during the testing of the reference fossil diesel (between tests of the vegetable oils), and so a linear relationship between the order in which the vegetable oils were tested and the increase in the in-cylinder pressure prior to SOC is perhaps not to be expected.

Fig. 3 shows the duration of ignition delay of the vegetable oils and reference fossil diesel at both constant injection and constant

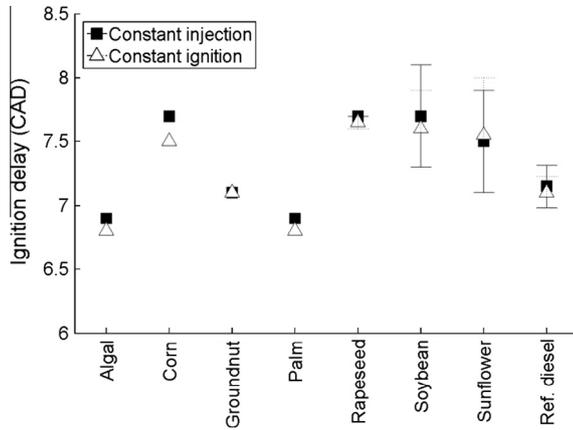


Fig. 3. Ignition delay (SOI to SOC) of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing.

ignition timings. In Fig. 3, and where present in the following figures, the limits of the error bars shown are plus and minus one standard deviation from the mean value (the value displayed on the plots), taken from repeat experimental runs of the same test fuel (up to a maximum number of nine repeats in the case of the reference fossil diesel). Notwithstanding the extent of the error bars present in Fig. 3, at both timing conditions, three of the vegetable oils, algal, groundnut and palm, displayed an ignition delay slightly shorter (~ 0.2 CAD) than the reference fossil diesel. The remaining four vegetable oils, corn, rapeseed, soybean and sunflower, exhibited a longer ignition delay (~ 0.5 CAD) than the reference fossil diesel at both timing conditions. All of the vegetable oils (except the algal oil for which comparable values are not available) possess a lower cetane number than the reference fossil diesel (Table 4) so it might have been expected that all of the vegetable oils would have displayed a longer ignition delay than the reference fossil diesel. However, considering only the vegetable oils, the two oils of highest cetane number (Table 4), groundnut and palm, both display a shorter ignition delay (Fig. 3) than all the oils (other than the algal oil for which no cetane number is available).

Fig. 4a and b show the peak apparent net heat release rate of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing. In Fig. 4a, it can be seen that at both timing conditions the reference fossil diesel exhibits a significantly higher peak heat release rate than any of the vegetable oils. In a previous study of single component alkane and alkene fuels [28], a strong correlation was found between the duration of ignition

delay and the peak heat release rate. It was observed that an increasing duration of ignition delay allowed more time for fuel and air mixing prior to SOC, resulting in a larger premixed combustion fraction and a higher peak heat release rate. No such relationship is visible when considering the peak heat release rate of the vegetable oils relative to the reference fossil diesel (Fig. 4a), with the latter displaying a duration of ignition delay (Fig. 3) within the range of those exhibited by the vegetable oils. In Fig. 4b, notwithstanding the extent of the error bars present, considering the peak heat release rates of the vegetable oils relative to one another, no clear relationship between duration of ignition delay (Fig. 3) and the peak heat release rates can be seen (Fig. 4b). This, and the much higher peak heat release rates of the reference fossil diesel relative to the vegetable oils (Fig. 4a), would suggest that in the case of the vegetable oils, duration of ignition delay is not the limiting factor on the rate of fuel and air mixing. Therefore, the influence of vegetable oil physical properties, such as boiling point and viscosity, on combustion phasing is explored in Section 3.2.

Fig. 5a and b shows the calculated maximum in-cylinder global temperature and time of occurrence of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing. In-cylinder global gas temperatures were calculated utilising in-cylinder pressure data and calculated values of the total cylinder volume at a given crank angle degree while assuming the cylinder contents to be a homogenous ideal gas. At both timing conditions, it can be seen that the reference fossil diesel exhibited a significantly higher maximum in-cylinder global temperature than all of the vegetable oils (Fig. 5a). This correlates with the higher peak heat release rate of the reference fossil diesel relative to the vegetable oils (Fig. 4a), and it follows that a more concentrated release of energy near TDC (Fig. 2), with lower levels of heat transfer to the cylinder walls, would result in a higher magnitude of maximum in-cylinder temperature (Fig. 5a). Considering the magnitude of maximum in-cylinder temperature of the vegetable oils relative to one another (Fig. 5a), an effect of peak heat release is not readily apparent (Fig. 4b).

In Fig. 5b, it can be seen that at both timing conditions, the reference fossil diesel reached the maximum in-cylinder temperature earlier than all of the vegetable oils. This can be attributed to the lower heat release rates of the vegetables oils (Fig. 4a), and a greater proportion of energy release during the diffusion controlled combustion phase (Fig. 2).

Fig. 6a and b shows the NO_x emissions of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing. At both timing conditions, it can be seen that the reference fossil diesel emitted significantly higher levels of NO_x than all of

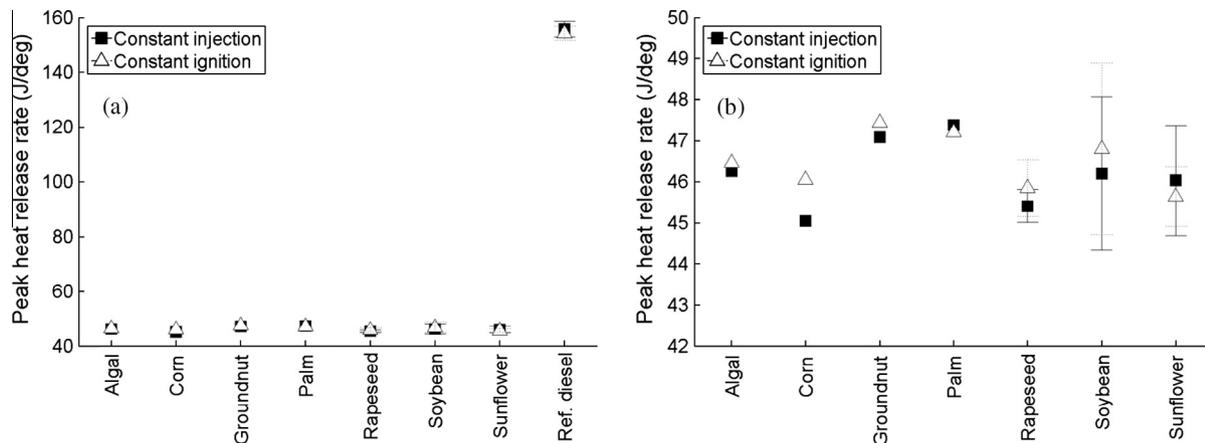


Fig. 4. Peak apparent heat release rate of (a) the vegetable oils and reference fossil diesel and (b) the vegetable oils only, at constant injection and constant ignition timing.

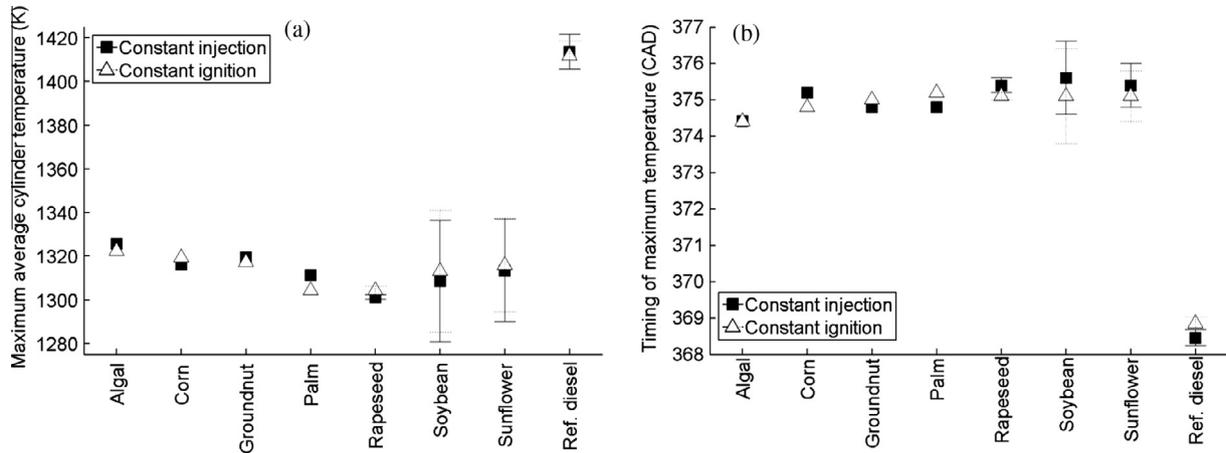


Fig. 5. (a) Calculated maximum in-cylinder global temperature and (b) time of occurrence of maximum global temperature of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing.

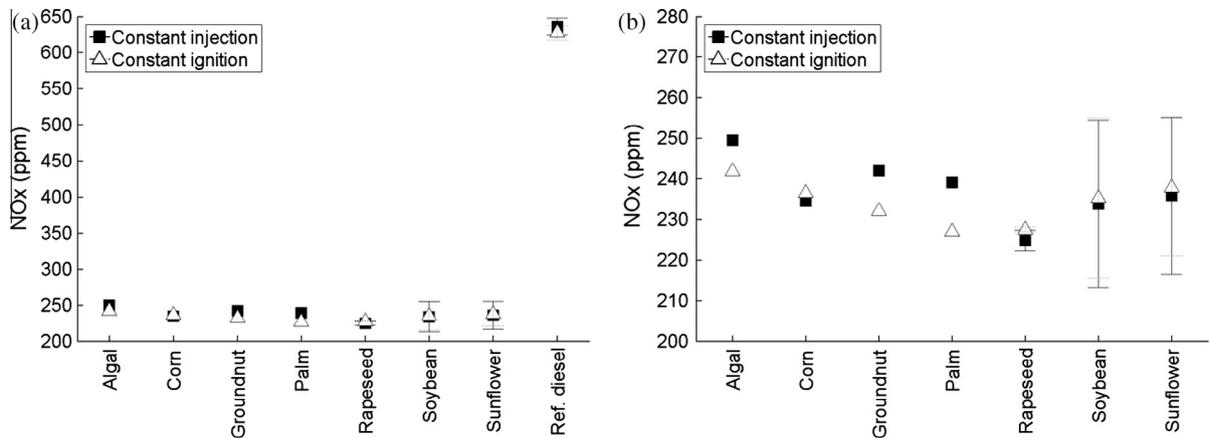


Fig. 6. NO_x emissions of (a) the vegetable oils and reference fossil diesel and (b) the vegetable oils only, at constant injection and constant ignition timing.

the vegetable oils (Fig. 6a). Production of NO_x in compression ignition engines is primarily by the thermal oxidation of nitrogen, the reaction rate of which increases with increasing in-cylinder temperatures and the residence time of the cylinder contents at elevated temperatures [31–33]. Thus the high NO_x emissions of the reference fossil diesel (Fig. 6a) are in agreement with the observed larger magnitude (Fig. 5a) and earlier time of maximum in-cylinder temperature (Fig. 5b) of the reference fossil diesel relative to the vegetable oils. Considering only the NO_x emissions of the vegetable oils (Fig. 6b), an influence of the in-cylinder thermal conditions is also apparent. The algal and rapeseed oils emitted the highest and lowest levels of NO_x respectively (Fig. 6b), and also displayed the highest and lowest maximum in-cylinder temperatures respectively (Fig. 5a). The lower NO_x emissions of the vegetables oils relative to the reference fossil diesel have been previously reported in engine tests of vegetable oils [15].

Fig. 7a and b shows the CO and THC emissions of the vegetable oils and reference fossil diesel at both constant injection and constant ignition timing. At both timing conditions, all of the vegetable oils emit significantly higher levels of both CO (Fig. 7a) and THC (Fig. 7b) than the reference fossil diesel. Both CO and THC are known products of incomplete combustion, the levels of which could be expected to be higher at the lower maximum in-cylinder temperatures displayed by the vegetable oils relative to the reference fossil diesel (Fig. 5a). An effect of injection timing is apparent in the emissions of CO and THC (Fig. 7a and b), with levels of both

higher for all of the vegetable oils at constant ignition timing. As there is no comparable trend of maximum in-cylinder temperature with injection timing, this would suggest a significant sensitivity of the vegetable oil and air mixing to the cylinder volume and turbulence conditions near TDC. This sensitivity is most apparent in the THC emissions of the vegetable oils (Fig. 7a); the largest offsets with injection timing are exhibited by the algal and palm oils, which displayed the shortest ignition delays of the oils (Fig. 2) and thus experienced the greatest shifts in combustion phasing at constant ignition timing relative to constant injection timing. It is hypothesised that the higher levels of both CO and THC (Fig. 7a and b) at constant ignition timing might be attributable to a greater level of piston fuel impingement at this timing, where a SOI closer to TDC would reduce the distance between the injector nozzle and piston bowl. The higher CO emissions of the vegetable oils relative to the reference fossil diesel (Fig. 7a) are similar to those reported by Altin et al. [17] in engine testing of vegetable oils heated to 80 °C.

Fig. 8a and b shows the particulate emissions of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing. Immediately apparent, at both timing conditions (Fig. 8a and b), is the lower number of ultrafine particles (D_p < 10 nm) but higher numbers of both nucleation mode (D_p < 50 nm) particles and accumulation mode particles emitted by the vegetable oils relative to the reference fossil diesel. This is likely to be due to the higher viscosity of the vegetable oils

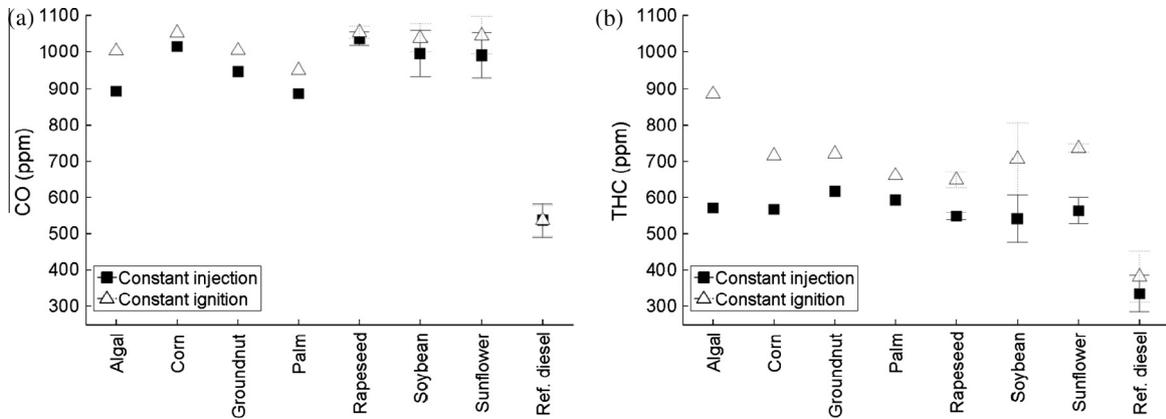


Fig. 7. (a) CO and (b) THC emissions of the vegetable oils and reference fossil diesel at constant injection and constant ignition timing.

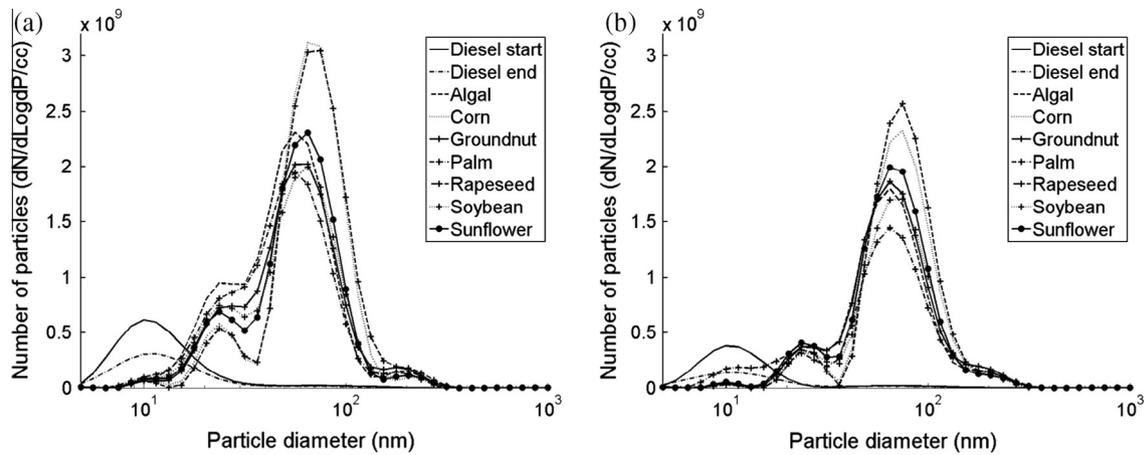


Fig. 8. Particulate emissions of the vegetable oils and reference fossil diesel at (a) constant injection and (b) constant ignition timing.

compared to the reference fossil diesel, which could be expected to adversely affect fuel atomisation, creating fuel rich zones required for particulate production [34]. At both timings (Fig. 8a and b), the highest peaks in particulate number are produced by the corn and rapeseed oils, while the palm and soybean oils consistently produce the lowest peaks. An effect of injection timing, is however apparent, with peak numbers of both nucleation and accumulation mode particles lower for all vegetable oils lower at constant ignition timing (Fig. 8b) than at constant injection timing (Fig. 8a).

Fig. 9 shows the total particulate mass emitted by the vegetable oils and reference fossil diesel at both timing conditions. The emission of particulate mass by the reference fossil diesel (Fig. 9) is an order of magnitude lower than that of all the vegetable oils, and can be attributed to the significant production of large accumulation mode particles by the vegetable oils (Fig. 8a and b). At both timing conditions (Fig. 9), the lowest particulate mass is emitted by the palm oil and the highest by the rapeseed and sunflower oils, and when considering only the vegetables oils it can be seen that emissions of particulate mass increase with duration of ignition delay (Fig. 3). Exhaust emission of soot is known to be sensitive to in-cylinder temperatures [34], as rates of soot oxidation increase with temperature. However, no clear effect of ignition delay (Fig. 3) was visible on either the magnitude or time of occurrence of maximum in-cylinder temperature of the vegetable oils (Fig. 5a and b). Furthermore, in the case of the vegetable oils, and as was observed in emissions of CO and THC (Fig. 7a and b), cylinder geometry at SOI may be a significant factor as emissions of total particulate mass are higher for all vegetable oils at constant ignition timing

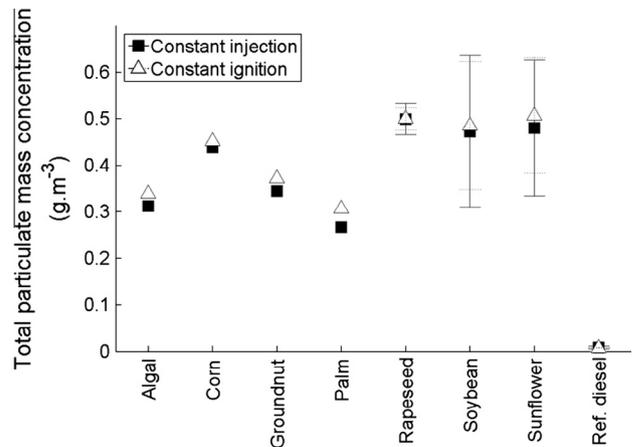


Fig. 9. Total particulate mass emitted by the vegetable oils and reference fossil diesel at constant injection and constant ignition timing.

(Fig. 9), despite no obvious correlation with in-cylinder thermal conditions (Fig. 5a and b).

3.1. Effect of vegetable oil fatty acid composition on low temperature reactivity

Many studies of both fatty acids and fatty acid esters have shown the structure of the alkyl chain of the fatty acid to be

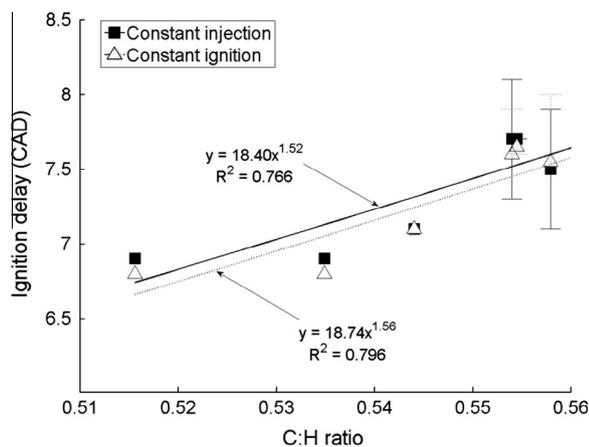


Fig. 10. Ignition delay of the vegetable oils as a function of carbon to hydrogen (C:H) ratio at constant injection and constant ignition timing.

important in determining the ignition quality of the molecule as a whole [7,31,33,35–40].

Fig. 10 shows the ignition delay of the vegetable oils as a function of the carbon to hydrogen ratio at both constant injection and constant ignition timing. Fig. 10 also shows a curve fit at constant injection timing corresponding to the expression $y = 18.40x^{1.52}$ with an R^2 value of 0.766. Such expressions are shown only where the confidence level has been determined as 96% or higher. The form of the regression equation used $Y = Ax^b$ allows the exponent b to provide a measure of the impact x has on Y (e.g. ignition delay), because $\frac{dY}{dX} = \frac{bY}{X}$. This means that a 1% change in x will cause a $b\%$ change in Y , and so in Fig. 10 for every 1% increase in the carbon to hydrogen, the ignition delay reduces by 1.5%. The carbon to hydrogen (C:H) ratio (Table 2) for each vegetable oil was determined by elemental analysis. In Fig. 10, it can be seen that at both timing conditions, increasing the vegetable oil C:H ratio increases the duration of ignition delay. Shortening the fatty acid alkyl chain length, or the introduction of further double bonds to the fatty acid alkyl chain, would both increase the C:H ratio which has been observed in the case of the fatty acid esters to increase the duration of ignition delay [31].

Fig. 11a and b shows the ignition delay of the vegetable oils as a function of average vegetable oil carbon chain length and number of double bonds (Table 2). It can be seen that increasing carbon chain length (Fig. 11a) and number of double bonds (Fig. 11b) both correlate with an increasing duration of ignition delay, though it

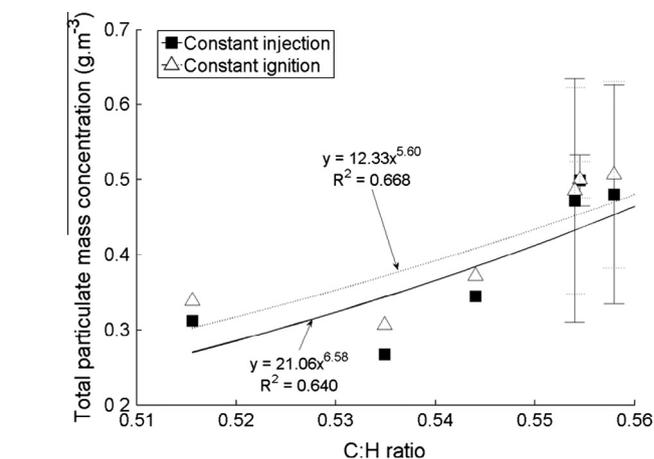
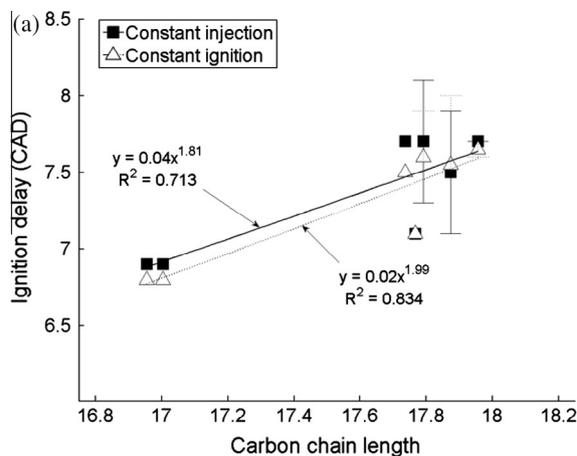


Fig. 11. Ignition delay of the vegetable oils as a function of (a) carbon chain length and (b) number of double bonds at constant injection and constant ignition timing.

Fig. 12. Total particulate mass emitted by the vegetable oils as a function of carbon to hydrogen ratio at constant injection and constant ignition timing.

should be noted that the R^2 values present are not representative of the degree of test variability as indicated by the error bars present. Increasing the number of double bonds in an alkyl chain, has previously been observed to increase the duration of ignition delay in both un-branched alkanes [28] and fatty acid esters [31], while an increase in the total number of double bonds present has also been observed to decrease the cetane number of vegetable oils [27]. Thus the suggested correlation between ignition delay and number of double bonds in Fig. 11b is supported by these previous observations and can be attributed to the influence of double bonds within alkyl chains on the low temperature reactivity of such structures. During the ignition delay period of compression ignition combustion, escalation of temperatures and propagation of radical species towards SOC is primarily driven by the oxidation and isomerisation of alkyl chains [41]. Internal isomerisation of an alkyl chain requires the formation of a six or seven member transition state ring, and such rings can only be formed by a chain of at least three fully saturated carbon atoms [41,42]. Therefore, it follows that an increased presence of double bonds will reduce rates of low temperature branching reactions and thus increase the duration of ignition delay.

The observed relationship between chain length and ignition delay (Fig. 11a), is however, (and notwithstanding the magnitude of error presented) potentially the inverse of what might be expected. Previous studies have found that where other features of molecular structure have been held constant, increasing the straight alkyl chain length reduces ignition delay [28,31], due to

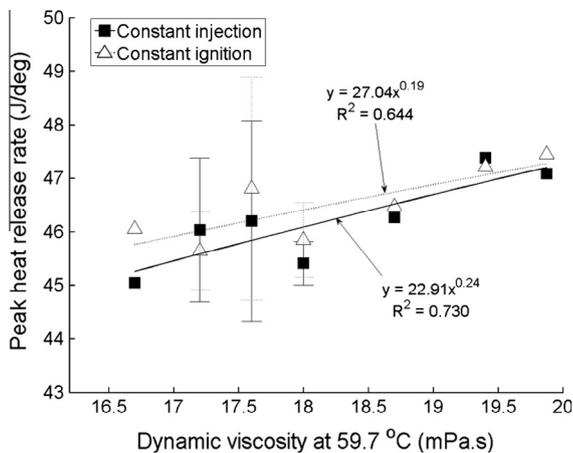


Fig. 13. Apparent peak heat release rate of the vegetable oils as a function of dynamic viscosity at 59.7 °C at constant injection and constant ignition timing.

the availability of more easily abstractable secondary H atoms that increase rates of low temperature branching reactions [41]. However, in the case of the vegetable oils, and as can be seen in Table 2, in general increasing alkyl chain length coincides with an increasing number of double bonds. For example, the algal and palm oils, which exhibited the shortest duration of ignition delay (Fig. 3), have a high content of saturated palmitic acid (C16:0) and oleic acid, whereas the sunflower and soybean oils, which exhibited the longest duration of ignition delay (Fig. 3), are nearly exclusively made up of oleic and linoleic acids (C18:1 and C18:2). Therefore, the trend in Fig. 11a is in fact also representative of the number of double bonds present, suggesting that the presence of double bonds in the fatty acids has more of an impact on ignition delay than average carbon chain length and is in agreement with the observations of Mehta and Anand [27]. It is also tentatively suggested that the lower R^2 values of the correlation of carbon chain length to ignition delay relative to that of number of double bonds to ignition delay (0.713 and 0.834 compared to 0.810 and 0.894), is therefore perhaps indicative of the expected counter-influence of carbon chain length; that is given an equal degree of saturation, increasing carbon chain length would decrease ignition delay. A more accurate determination as to the influence of vegetable oil alkyl chain length might be ascertained by considering only the saturated alkyl chain length, however, such analysis was considered unreliable without more detailed analysis of the vegetable oil composition.

Fig. 12 shows the total particulate mass emitted by the vegetable oils as a function of the carbon to hydrogen ratio at both constant injection and constant ignition timing. It can be seen from Fig. 12, as either the alkyl chain length or degree of saturation decreases, the level of particulates emitted increase. This is to be expected given the observed correlation between C:H ratio and the duration of ignition delay (Fig. 10), and the concurrent increase in particulate emissions (Fig. 9) with duration of ignition delay (Fig. 3). However, this effect of ignition delay (Fig. 3) cannot be attributed to in-cylinder thermal conditions (Fig. 5a and b) and thus rates of soot oxidation. Therefore, it is suggested that the increasing number of double bonds present with increasing C:H ratio primarily results in greater initial soot production, and that any influence of combustion phasing on soot oxidation rates is secondary; the presence of double bonds is known to increase the sooting tendency of a fuel molecule [43].

3.2. Effect of vegetable oil fatty acid physical properties

Fig. 13 shows the apparent net peak heat release of the vegetable oils as a function of dynamic viscosity at 59.7 °C at both con-

stant injection and constant ignition timing. Increasing dynamic viscosity correlates with increasing peak heat release rate (Fig. 13) at both injection timings, though the correlation is stronger at constant injection timing (R^2 of 0.730 relative to 0.644). This is somewhat counter-intuitive, in general it could be expected that an increase in fuel viscosity would result in larger droplet sizes upon atomisation, and thus reducing rates of fuel vaporisation and subsequent mixing of air. The peak heat release of the fuels, via the premixed burn fraction, can be considered to be a function of the time available for fuel and air mixing (fuel ignition delay) and the rate at which it occurs. Increased viscosity could therefore be expected to reduce peak heat release rate by both reducing the rate of fuel and air mixing and the duration of ignition delay; increased alkyl chain length and degree of saturation both increase viscosity [26] and reduce ignition delay (Section 3.1). The reduced rates of fuel and air mixing may account for the significantly lower peak heat release rate of the vegetable oils relative to the reference fossil diesel (Figs. 2 and 5a), where the viscosity of reference fossil diesel is an order of magnitude lower than that of the vegetable oils (Table 4). However, the absence of such a trend in Fig. 13, would therefore suggest that above a threshold viscosity, the duration of ignition delay is not of primary importance in determining the peak heat release rate. It would also suggest that the oil droplet size is not the primary impact of viscosity on the rate of vegetable oil and air mixing at the conditions presented.

Possible relationships between other physical properties that may influence fuel droplet size and fuel air mixing were investigated (density and surface tensions); however, the correlations found were weak relative to that displayed by viscosity and peak heat release rate ($R^2 < 0.513$ relative to $R^2 > 0.644$). Ryan et al. [5] and Deshmukh et al. [25] both observed that increasing vegetable oil viscosity reduced the spray penetration rate, and it is suggested that this phenomenon may account for the reduction in peak heat release rate with decreasing viscosity observed in Fig. 13. Namely, it is hypothesised that in the case of all the vegetable oils a degree of fuel impingement on the piston bowl and cylinder walls is occurring and that this reduces the rate of fuel and air mixing. Therefore, where an increase in vegetable oil viscosity reduces the spray penetration rate, the incidence of fuel impingement on the piston bowl and cylinder walls will decrease also. Subsequently, the efficiency of fuel and air mixing is improved (due to a reduced level of fuel impingement), and the extent of the premixed burn fraction and the peak heat release rate increases. Such a hypothesis is supported by the stronger correlation of peak heat release rate at constant injection timing than at constant ignition timing (Fig. 13), as at the former condition all fuels would be subject to the same initial dynamic cylinder geometry. It is also tentatively suggested that this may partially account for the extent of cycle to cycle variability exhibited by the sunflower and soybean oils (Figs. 5b and 13), as a greater degree of fuel impingement may increase the sensitivity of combustion phasing to cylinder wall heat transfer. It should however be noted that this suggested influence of vegetable oil viscosity may well vary with increasing fuel injection pressures, as several previous studies have observed increased levels of complete fuel combustion (as indicated by reduced emissions of CO and THC, and attributable to improved fuel air mixing) and also fuel spray penetration length with increasing fuel injection pressures [44–46].

An influence of fuel impingement on the significantly higher peak heat release rate displayed by the reference fossil diesel relative to the vegetable oils (Fig. 4a) is also suggested. Assuming that a degree of fuel impingement also occurs in tests with the reference fossil diesel, it can be seen that the higher boiling points of the vegetable oils relative to the reference fossil diesel (as indicated by the relative flash points in Table 4) will exacerbate the negative impact of fuel impingement on fuel and air mixing. With higher boiling

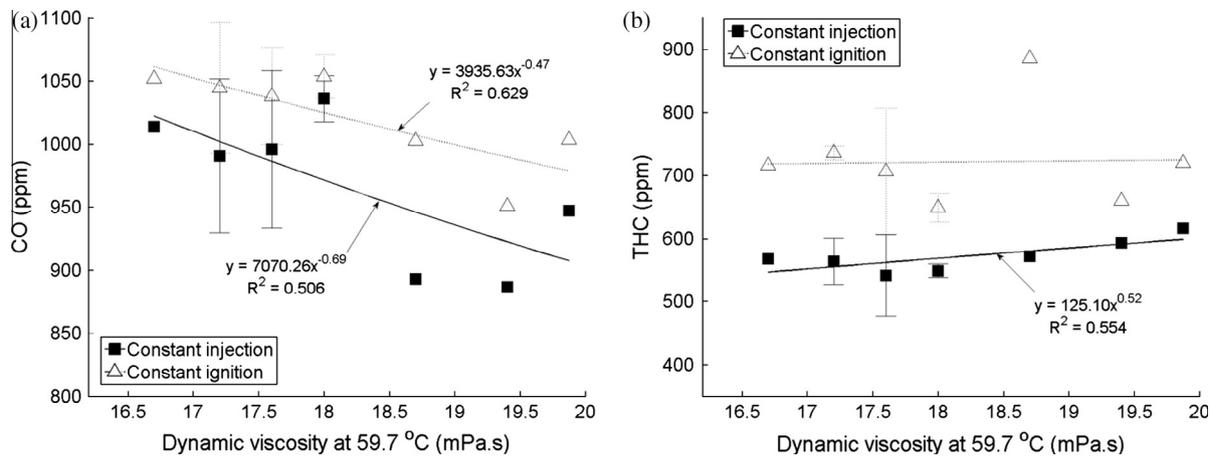


Fig. 14. (a) CO and (b) THC emissions of the vegetable oils as a function of dynamic viscosity at 59.7 °C at constant injection and constant ignition timing.

points, the vegetable oils will require higher local temperatures than the reference fossil diesel for vaporisation of fuel present on the cylinder walls, and so it could be expected that the impinged vegetable oils will be available for combustion somewhat later than the impinged reference fossil diesel.

Fig. 14a and b shows the CO and THC emissions of the vegetable oils as a function of dynamic viscosity at 59.7 °C at both constant injection and constant ignition timing. At both timing conditions, levels of CO emitted increase with decreasing viscosity (Fig. 14a), with the trend stronger at constant ignition timing, with the correlation described by an R^2 value of 0.620 relative to that of 0.506 at constant injection timing. At constant injection timing, levels of THC increase with increasing dynamic viscosity (Fig. 14b), while it is not possible to clearly discern a trend at constant ignition timing. The increase in CO emissions with decreasing vegetable viscosity (Fig. 14a) supports the hypothesis that levels of fuel impingement increase with decreasing viscosity; an increase in cylinder wall and piston bowl fuel impingement would likely result in a greater degree of incomplete combustion via both lower global peak heat release rates (Fig. 13) and local temperatures.

Fig. 15 shows the total particulate mass emitted by the vegetable oils as a function of dynamic viscosity at 59.7 °C at both constant injection and constant ignition timing. Notwithstanding the range of error shown (Fig. 15), it can be seen that reducing viscosity increases the total particulate mass produced at both timing conditions. While the R^2 values of the relationships found between total particulate mass and dynamic viscosity (Fig. 15, $R^2 = 0.588$ and 0.595 at constant injection and constant ignition timing respectively) are somewhat lower than those with C:H ratio (Fig. 12, $R^2 = 0.640$ and 0.668 at constant injection and constant ignition timing respectively), they are higher than the value of R^2 found when investigating the relationship between dynamic viscosity and C:H ratio ($R^2 = 0.418$). Therefore, while secondary to the C:H ratio of the vegetable oils, an influence of viscosity on soot production is plausible. With regards to the suggestion that decreasing vegetable oil viscosity increases fuel impingement, concurrent lower peak heat release rates and local temperatures may both reduce rates of soot oxidation, and thus increase particulate emissions. However, in general, soot emissions are found to increase under fuel rich conditions [34], which might be expected to be more prevalent where fuel droplet sizes are potentially larger due to increased fuel viscosity. Therefore, the presence of a correlation between increasing particulate matter and decreasing fuel viscosity, would suggest that the effect of vegetable oil cylinder wall and piston bowl impingement is of more significance than vegetable oil droplet size. It is hypothesised that by the time the

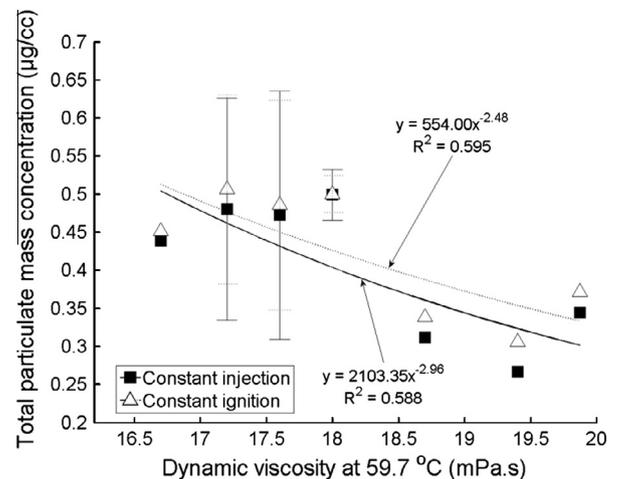


Fig. 15. Total particulate mass emitted by the vegetable oils as a function of dynamic viscosity at 59.7 °C at constant injection and constant ignition timing.

vaporisation of fuel impinged on the cylinder wall during the expansion stroke, after local temperatures have been raised sufficiently by the combustion of fuel not impinged, in-cylinder temperatures may remain hot enough for the formation of soot but not for subsequent oxidation of particulate matter. Therefore, it follows that reduced vegetable oil viscosity, resulting in an increased level of fuel cylinder wall impingement, will see an increase in the level of fuel present at these cooler in-cylinder conditions with a subsequent increase in exhaust gas levels of particulate matter.

4. Conclusions

1. At a fuel temperature of 60 °C, in a direct injection compression ignition engine, seven straight vegetable oils were found to exhibit durations of ignition delay similar to that of a reference fossil diesel. However, the peak heat release exhibited by the vegetable oils was significantly lower than that of the reference fossil diesel, suggesting the oil physical properties to be more important in determining the fuel premixed fraction than the duration of ignition delay.
2. The ignition delay of the vegetable oils was found to correlate well with the carbon to hydrogen ratio of the constituent fatty acids, indicating that the ignition delay of the vegetable oils was

- dictated by the molecular structure and thus low temperature reactivity of the fatty acid alkyl chains.
- The significantly lower peak heat release rates of the vegetable oils relative to the reference fossil diesel can be attributed to the substantially higher viscosities of the former impacting on the efficiency of fuel and air mixing during the ignition delay period. Reduced efficiency of fuel and air mixing reduces the extent of the premixed burn fraction, and thus the peak heat release rate. However, considering only the vegetable oils, decreasing viscosity correlated with reduced peak heat release rate. It was hypothesised that decreasing vegetable oil viscosity increased fuel cylinder wall and piston bowl impingement, negatively affecting the efficiency of fuel and air mixing.
 - All of the vegetable oils emitted significantly lower levels of NO_x than the reference fossil diesel. This is in agreement with observed peak heat release rates, and thereby reduced production of NO_x by the thermal mechanism.
 - Emissions of CO and THC were higher for all of the vegetable oils relative to the reference fossil diesel, and showed a clear effect of injection timing. Furthermore, increasing levels of CO were found to correlate with decreasing vegetable oil viscosity. This trend and the observed offset in emissions of CO and THC with injection timing, were both in agreement with the hypothesised increase in fuel impingement with decreasing vegetable oil viscosity.
 - Relative to the reference fossil diesel, particulate emissions of the vegetable oils were much higher and can be attributed to higher viscosities of the oils reducing in-cylinder temperatures, and thus rates of soot oxidation, and also reducing the efficiency of fuel atomisation and increasing the presence of fuel rich zones within the cylinder charge. However, considering only the vegetable oils, increasing levels of particulate mass correlated with increasing oil C:H ratio and to a lesser extent decreasing oil viscosity. This suggests the presence of double bonds and the effects of fuel impingement to be of more importance in determining soot levels than local fuel air stoichiometry.

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