The influence of fatty acid ester alcohol moiety molecular structure on diesel combustion and emissions

Paul Hellier*[a], Nicos Ladommatos[a], Robert Allan[b], John Rogerson[b]

[a] Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

[b] BP Fuels and Lubricants Technology, BP Technology Centre, Whitchurch Hill, Pangbourne, Reading, RG8 7QR, United Kingdom

Corresponding author: Paul Hellier

Postal address: Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

Email: p_hellier@meng.ucl.ac.uk or hellier.pr@gmail.com

Telephone: +4420 7679 0011

Fax: +44 20 7388 0180

Abstract

At present, biodiesel primarily comprises of fatty acid methyl esters (FAMEs) obtained by the transesterification of a variety of vegetable oils with methanol. However, transesterification can be carried out with a wide variety of alcohols other than methanol. This paper presents experimental studies carried out on a diesel engine supplied with a range of single-molecule fuels to investigate the effect of fuel molecular structure on combustion and emissions. Eight fatty acid esters which can be produced by transesterification of vegetable oils and animal fats using methanol, ethanol, n-propanol, n-butanol, iso-propanol, iso-butanol and tert-butanol were investigated. The aim was to ascertain the way in which the structure of the alcohol reactant and the corresponding moiety in the ester molecule affects combustion and emissions. Previously obtained experimental results from a second set of 18 non-oxygenated acyclic hydrocarbons were used to assist the interpretation of the test results from the eight fatty acid esters. The engine tests were carried out at constant injection timing and they were repeated at constant ignition timing and at constant ignition delay, the latter being achieved through the addition to the various fuels of small quantities of ignition improver (2- ethyl hexyl nitrate). Only small differences in ignition quality of the fatty acid esters were found with variation of the molecular structure of the alcohol moiety. Where present, differences in ignition delay were found to be the main driver of both combustion phasing and emissions production. With the effect of ignition delay isolated physical properties of the esters, such as thermal degradation prior to vaporisation and boiling point, were found to exert an influence on levels of particulate and NOx emissions.

Keywords: biodiesel, fatty acid ester, molecular structure, alcohol moiety, emissions, thermal degradation

1. Introduction

Future fuels will increasingly be derived from a diverse range of fossil and renewable sources and must be designed to ensure that their production and use in combustion systems will be sustainable[1-5]. In addition to the need for mankind to react to the potential dangers of climate change posed by anthropogenic release of CO_2, other damaging pollutants formed during combustion, such as nitrous oxides and soot, are continuously subject to stricter controls which are designed to limit adverse environmental impacts[6-8]. As the impetus to mitigate these impacts intensifies, every aspect of a fuel's lifecycle, from sourcing of feed-stocks to eventual use, must come under increasing scrutiny to ensure long-term sustainability.

Since the initial development of biodiesel, methanol has been the most widely used alcohol for the process of transesterification, and in 1999 some 90% of the methanol produced was from natural gas[9] by means of steam reformation. However, if considering a bio-fuel to truly be an alternative to fossil fuels the use of either natural gas or coal (which is another suitable feedstock for methanol production via steam reformation) would be inappropriate.

Alternative alcohols to methanol have been available via production from biomass for some time, and the combustion and emissions characterization of stearic acid esters produced from such alcohols forms the subject of this paper. Due to use as a substitute for gasoline, ethanol has been produced industrially from biomass since the early 20th century by means of fermentation and distillation processes utilizing primarily agricultural feed-stocks (sugar cane in Brazil and corn in the USA)[10]. Batch methods for the production of longer chain alcohols from biomass have also been utilized industrially, albeit to a lesser extent. Continuous iso-propanol, butanol and ethanol (IBE) fermentation has been successfully conducted by the immobilisation of the bacteria *Clostridium beijerinckii* in a substrate of glucose and yeast[11]. However, at the time of the investigation (1983) several technical deficiencies of the reactor limited solvent production.

The anaerobic bacteria *Clostridium acetobutylicum* can also be used to convert biomass through combined acetone-butanol-ethanol (ABE) fermentation. Recent increased viability of butanol

production by this process can be attributed to the development of new methods of continuous fermentation that do not result in the destruction of the bacteria on product recovery and leave immobilised cells in-situ (gas stripping, liquid to liquid extraction using a selective solvent, or pervaporation where butanol in vapour form is made to diffuse through a membrane)[12]. Recently large petroleum companies have invested in production of butanol from biomass and several butanol production facilities are under development[13,14].

Base catalyzed transesterification (the industrial norm for fatty acid ester production) is generally unsuitable for use with longer chained alcohols[15]. However, there are alternative methods of transesterification for which long chain alcohols are superior to methanol. Transesterification under supercritical conditions allows the reaction to occur in the absence of a catalyst, resulting in a high purity of both products and excess reactants[16]. Long chain alcohols are more suitable for supercritical transesterification as they have higher boiling points and so lower pressures are reached when conducting reactions in a closed vessel.

Acid catalyzed transesterification can be preferable to base catalyzed as in addition to triglycerides free fatty acids also undergo conversion. Transesterification with an acid catalyst has given yields 30% greater from n-propanol, n-butanol and iso-propanol relative to methanol[17]. It is suggested that the hydrophobic nature of the longer chained alcohols increases miscibility in oil and thus the level of mixing. Additionally, the higher boiling point of these alcohols also allows for the reaction to take place under higher temperatures.

The effect on diesel combustion and emissions of increasing the carbon chain length of the fatty acid moiety of an ester has been observed many times, with an increase in the chain length found to improve the ignition quality of the fuel[15,18]. However, the impact of increasing the alcohol moiety has been less well understood. Knothe et al.[19] reported on the cetane numbers of esters of varying alcohol moiety carbon chain length and fatty acid moiety saturation. The cetane numbers of methyl, ethyl, propyl and butyl esters of stearic (C18:0 and engine tests of which are included in this paper), oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acid, and also the pure acids, were determined by Ignition

Quality Testing (IQT), with all components possessing a stated purity in excess of 99%. The relationship between cetane number and carbon chain length in the alcohol moiety was, however, not linear in most cases. For example, the methyl esters of linoleic acid exhibited a higher cetane number than both the ethyl and propyl esters of linoleic acid. Serdari et al.[20] similarly measured blended cetane numbers of methyl to butyl esters of various fatty acids, oleic (C18:1), palmitate (C16:0), myristate (C14:0) and laurate (C12:0). While for all the fatty acids butyl esters consistently possessed a higher BCN than those prepared with shorter chain alcohols, again there was no linear trend between cetane number and alcohol carbon chain length.

In engine drive cycle tests, Makareviciene and Janulis[21] compared emissions from pure RME to those from REE and found the ethyl ester to produce lower emissions of NOx and CO, but an increased level of unburnt hydrocarbon emissions relative to the methyl ester of identical fatty acid moiety. During engine tests, Lapuerta et al.[22] found no discernable difference in the ignition delay of methyl and ethyl esters prepared from waste cooking oil. A slight decrease in NOx levels with the increased alcohol moiety chain length was detected and suggested by the authors to be either attributable to the reduced oxygen content or an unseen higher ignition quality of the ethyl ester. More significant were observed reductions in the level of un-burnt hydrocarbons emitted by the ethyl ester relative to the methyl, and lower smoke opacity, particulate mass and mean particle size produced by the methyl ester relative to the ethyl. These emissions characteristics were found to correlate well, but not exclusively, with fuel oxygen content.

Schönborn et al.[18] investigated the combustion and emissions of single component fatty acid ester fuels in a single cylinder direct injection common rail diesel engine at low loads. Increasing the alcohol chain length from one to two saw a small increase in ignition quality and a lower peak heat release rate. With ignition delay removed as a variable the ethyl ester produced lower emissions of NOx but an increased total mass of particulates compared to the methyl ester. It was suggested that atomization of the ethyl ester suffered due to an elevated melting point relative to the methyl ester, and this contributed to the increase in the total mass of particulates. The lower oxygen content of the ethyl ester

and soot formation pathways specific to the ethyl alcohol moiety were also mooted as possible causes of the increase.

Zhang et al. investigated, in two studies[23,24], the influence of fatty acid ester molecular structure on ignition kinetics in a motored Cooperative Fuel Research (CFR) engine at very low loads with constant equivalence ratio. Increasing the alcohol chain length whilst keeping the fatty acid chain length constant (methyl nonanoate to ethyl nonanoate) was found to increase the low temperature reactivity of the ester. This was attributed to a combination of an increase in the number of easily abstracted secondary C-H bonds (which increases the rate of temperature escalation in the ignition delay period) when increasing the alcohol chain length, and the suggested potential of ethyl esters to undergo a six centered uni-molecular elimination reaction, which has a relatively low activation energy. The proposed six centered uni-molecular elimination reaction of ethyl esters sees their pyrolysis, via an intermediate cyclic structure, without the need for any radical addition or external hydrogen abstraction.

Kinoshita et al. [25] investigated the physical properties of palm oil fatty acid esters prepared with alcohols ranging from methanol to octanol. Pour points of methyl, ethyl, propyl and butyl esters were found to decrease with increasing alcohol moiety carbon chain length. When the alcohol moiety carbon number exceeded 4 pour points were found to increase with an increase in the length of the alcohol moiety. Methyl, ethyl, n-propyl and n-butyl palm oil esters were also combusted in a single cylinder diesel engine with combustion and emissions characterized. No differences in either ignition delay or heat release were detected between the fuels, but the propyl and butyl esters did show elevated THC, CO and smoke emissions relative to the shorter alcohol chain esters. The authors suggested this to be an effect of the lower oxygen content but higher kinematic viscosity and boiling point of the longer alcohol moiety esters, with all three properties impeding fuel and air mixing.

The use of branched alcohols in the production of fatty acid esters has received very little attention. Knothe et al.[26] expanded their study of cetane numbers of fatty acid esters to include the effect of branching in the alcohol component of an ester. The authors predicted that, as with alkanes, branching

of the carbon chain would reduce cetane number. However, results from the IQT measurements of ignition delay showed this not to be the case, with cetane numbers either increasing or remaining constant when introducing branching to the alcohol component and maintaining a constant number of carbon atoms. Kinoshita et al.[25] included an ester produced from iso-butanol in their study of palm oil esters with varying alcohol moiety. They found the peak heat release rate of the iso-butyl ester to be slightly higher than that of the esters with straight alcohol moieties and attributed this to a slightly longer ignition delay of the iso-butyl ester (0.1 CAD). Emissions of THC, CO were similar to those of the n-propyl and n-butyl esters, with smoke emissions closest to those of the n-butyl ester.

This paper presents the results of engine experiments in which a series of fatty acid esters were tested. The esters were chosen to investigate the effect of fatty acid ester alcohol moiety carbon chain length and branching on diesel combustion and emissions.

2. Experimental methods

2.1 Apparatus

All combustion experiments presented were conducted in a single cylinder direct injection diesel engine specially designed for combustion research. Many of the fuels tested were available in only small quantities at the high assay required, or had physical properties, such as low lubricity, which would have resulted in damage to the fuel pump and common rail components. In addition several of the fuels were solid at room temperature. So, to overcome these issues, a previously designed and manufactured[27], heated, low volume and high injection pressure fuel system was utilized.

Based on the concept first proposed and implemented by Schönborn et al.[28], the system uses the engine common rail system as a hydraulic fluid supply so as to pressurize a small quantity of the sample fuel (100 – 250 ml) via two free pistons. The redesigned system used for the tests discussed in this paper features a bypass operated by high pressure needle valves that allows fossil diesel fuel from the engine pump circuit to flow at pressure through the test fuel circuit. This allows the fuel system and combustion chamber to be flushed with a reference diesel between every test run. A schematic of the

system is given in Figure 1. The sample fuel was supplied to the engine fuel injector via a 1 μm sintered filter element. The injector nozzle had six holes, each of 154 μm diameter. The sample fuel lines and low volume fuel system were all held at a constant temperature, of up to 358 $\pm$ 2.5 K, by several heating elements divided into five zones, each controlled by a separate PID controller on account of the widely differing thermal properties of each zone. Further details of the engine and control apparatus are given in Table 1.
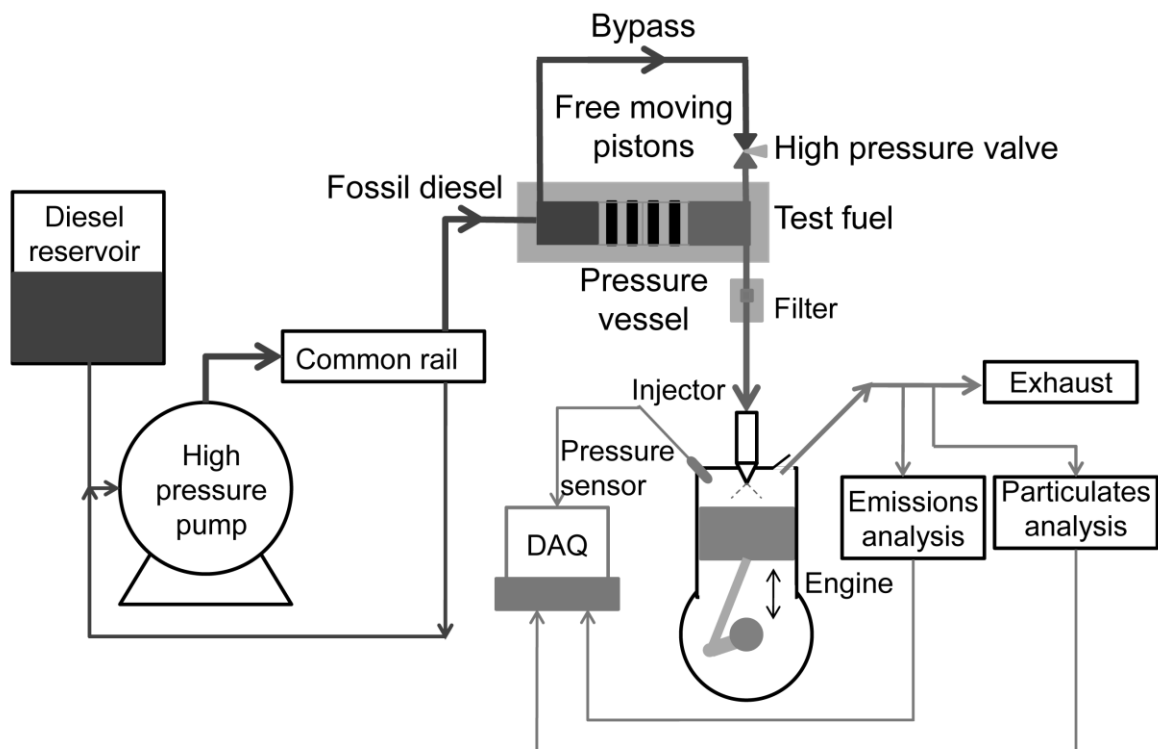
Figure 1. Schematic showing operation of the low volume fuel system.

The engine cylinder gas pressure was measured and logged with a PC data acquisition system (National instruments) at every 0.2 CAD using a piezoelectric pressure transducer (Kistler 6056AU38) and charge amplifier (Kistler 5011). At bottom-dead-centre of every combustion cycle the cylinder pressure was pegged by the data acquisition system using a piezoresistive pressure transducer (Druck PTX 7517-3257) located in the intake manifold, 160 mm upstream of the inlet valves. The normally aspirated engine had a geometric compression ratio of 15.8:1. For all the tests air was aspirated into the combustion chamber at atmospheric pressure and temperature. Various control and experiment temperatures were measured with K – type thermocouples and logged with the same PC data acquisition system utilized in recording in-cylinder pressures. The net apparent heat release rate was

derived from the measured in-cylinder pressure during post-processing (MATLAB), as were the global gas temperatures utilizing a one dimensional and one zone model assuming homogeneity and ideal gas behavior of the cylinder contents.

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	15 MPa
Peak motoring pressure at test conditions	3.6 MPa
Piston design	Central ω - bowl in piston
Oil temperature	353 ± 2.5 K
Water temperature	348 ± 2.5 K
Fuel injection pump	Single - cam radial - piston pump (BOSCH CP3)
High pressure fuel rail	Solenoid controlled, max. 160 MPa (BOSCH CRS2)
Injectors	6 - hole solenoid controlled (DELPHI DF1 1.3)
Electronic fuel injection system	1 μs accuracy (EMTRONIX EC-GEN 500)
Shaft encoder	0.2 CAD resolution

Exhaust gas sampling occurred 180 mm downstream of the exhaust valves to determine concentrations of gaseous species and also particulate size distribution. An automotive gas analyzer system (Horiba MEXA 9100 HEGR) was used to measure the following: NOx concentrations by chemiluminescence; CO and CO_2 concentrations with non-dispersive infrared; paramagnetic analysis to determine O_2 concentrations; and levels of un-burnt hydrocarbons were measured with a flame ionization detector. Size and mass distributions of the sub-micron particles in the exhaust gas were

determined by a differential mobility spectrometer (Cambustion DMS500). Sampling of exhaust gases for particulate measurements was made via a heated line with a dilution cyclone at the connection between the exhaust and heated line. Exhaust gases were diluted at this point by 4:1, and were diluted a second time upon entry to the analyser by 100:1. The heated line and both dilution cyclones were heated to a constant temperature of 328 K.

2.2 Fuel molecules investigated

A series of eight fatty acid esters were tested to assess the impact on combustion phasing and emissions production of two structural properties specific to the alcohol moiety of fatty acid esters:

1. Straight carbon chain length in the alcohol moiety

2. Carbon chain branching in the alcohol moiety

To observe the impact of increasing the straight carbon chain length of the alcohol moiety of a fatty acid ester, four esters of stearic acid were tested: methyl stearate (C19), ethyl stearate (C20), n-propyl stearate (C21) and n-butyl stearate (C22). A further three esters of stearic acid were tested to investigate the effect of carbon chain branching in the alcohol moiety: iso-propyl stearate (C21), iso-butyl stearate (C22) and tert-butyl stearate (C22). While esters of stearic acid are not particularly representative of the vegetable oils commonly utilized in the production of biodiesel (as they are fully saturated) they were chosen so to reduce the complexity of the chemical synthesis and thus ensure a high degree of purity. One additional fatty acid ester, methyl oleate (C19), a single n-alkane (C18) and reference fossil diesel (with zero FAME content) were also tested so as to allow an understanding of the relative importance of the two properties of alcohol moiety relative to other structural features of fatty acid esters.

Two of the fatty acid esters studied and one n-alkane (n-methyl stearate, n-ethyl stearate and n-octadecane) were obtained from a chemical supplier (Sigma Aldrich UK). All other molecules studied were specially synthesized by an organic synthesis company, with assay and other properties of each presented in Table 2; the molecular structure of each fuel is given in Table 3. The reference diesel used was fossil derived and contained no fatty acid esters.

In addition, experimental results from a second set of 18 non-oxygenated acyclic hydrocarbons were used to assist the interpretation of the test results from the eight fatty acid esters[27]. These were between C7 and C22 and were selected for an investigation and quantitative assessment of the effect of straight carbon chain length, degree of saturation and carbon chain branching on combustion phasing and emissions production in alkyl chains.

Table 2. Fuel properties.

	Molecular formula	Assay (%)	T_{boil} (K)	T_{melt} (K)	Cetane number [29]	Density at 60 °C (Kg/m^3)	Dynamic viscosity at 60 °C (mPa.s)	Lower heating value (MJ/Kg)
Reference fossil diesel	-	-	542‡	-	51.7•	834.5$^\phi$	-	43.14†
Methyl oleate	$C_{19}H_{36}O_2$	93.8	600.3*	252.94[30]	62.3	845.1[31]	2.638[31]	37.42†
Methyl stearate	$C_{19}H_{38}O_2$	96	601.8*	310.81[30]	88.9	835.3[31]	3.2252[31]	37.64[32]
Ethyl stearate	$C_{20}H_{40}O_2$	97	611.5*	306.13[30]	86.83	830.3[31]	3.3073[31]	37.79[32,33]
n-propyl stearate	$C_{21}H_{42}O_2$	98.4	620.8*	301.25[30]	80.4	829.6[34]	4.406[34]	37.72†
n-butyl stearate	$C_{22}H_{44}O_2$	98.3	629.6*	298.78[30]	86.3	-	-	38.40†
iso-propyl stearate	$C_{21}H_{42}O_2$	98.8	616.1*	301.55[35]	96.5	824.4[34]	4.355[34]	37.96†
iso-butyl stearate	$C_{22}H_{44}O_2$	99.3	625.2*	302.90[35]	99.3	-	-	38.06†
tert-butyl stearate	$C_{22}H_{44}O_2$	94.7	622.5*	305.05[36]	-	-	-	38.10†
n-octadecane	$C_{18}H_{38}$	99	589.3[37]	301.65[38]	106.3	755.8[39]	2.062[40]	43.90[41]

* = 2nd order calculations by the Constantinou and Gani method[42], † = calculated from experimental data obtained by the IP12 method[43], ϕ = experimental data obtained according to ASTM D4052 at 15 °C, • = experimental data obtained according to EN ISO 516, ‡ = experimental data obtained according to EN ISO 3405.

2.3 Experimental conditions

Each of the 8 molecules was initially tested at two experimental conditions: constant fuel injection timing and constant start of ignition timing. At constant injection timing the start of injection (SOI, defined as the time at which the injector actuating signal commences) was held constant at 7.5 CAD

BTDC, at which timing the reference fossil diesel was found to combust at approximately top-dead-centre (TDC) and start of combustion (SOC – defined as the minimum value of cumulative heat release after SOI and before the time of peak heat release rate) for each fuel varied according to the ignition delay of that fuel. For constant ignition timing, the SOI was varied so that the SOC of all fuels always occurred at TDC.

After the initial two sets of experiments at constant injection and constant ignition timing were completed, a third series of experiments was carried out during which the ignition delay of the different sample fuels was held constant (where differences in ignition delay between test fuels were recorded that were greater than the resolution of the shaft encoder used in measurement of in-cylinder pressure). This was achieved by adding the radical providing ignition improver (2 EHN) in small concentrations to each test fuel, in an iterative process to determine the correct dosage. These experiments at constant ignition delay were conducted at both a constant injection timing of 7.5 CAD BTDC and at a constant ignition time of TDC.

As some fuels were solid at room temperature, all fuels were first heated in a PID controlled water bath held at 358 ± 2 K prior to filling of the low volume fuel system which had been preheated to 358 ± 2 K and was held at this temperature throughout the subsequent experiment.

All tests were conducted at an engine speed of 1 200 rpm and at 45 MPa fuel injection pressure. The injection duration was adjusted in the case of every fuel, so that the engine IMEP was always constant at 0.4 MPa for all fuels. A summary of the engine and test operating conditions is given in Table 4.

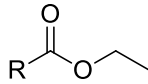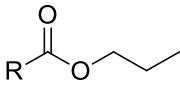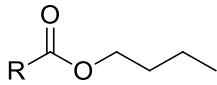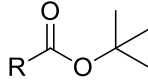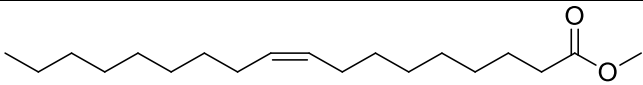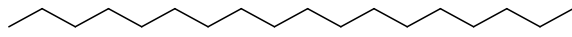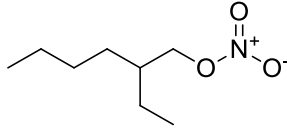Table 3. Fuel molecular structures.
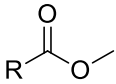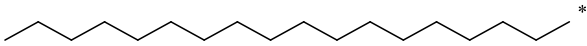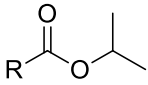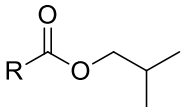
1. Straight carbon chain length in the alcohol moiety	**methyl stearate** **ethyl stearate** **n-propyl stearate** **n-butyl stearate**
Where R =	(long carbon chain) *
2. Addition of carbon chain methyl branches in the alcohol moiety	*iso*-propyl stearate *iso*-butyl stearate *tert*-butyl stearate
Importance of alcohol moiety relative to fatty acid saturation	methyl oleate
Importance of alcohol moiety relative to ester functional group	*n*-octadecane
Ignition improving additive	2 ethyl-hexyl nitrate

Table 4. Engine and test operating conditions.

Fuel	2 EHN dosage (ppm)	Engine speed (rpm)	Fuel injection pressure (MPa)	IMEP (MPa)	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	1 δ	Mean	1 δ	Mean	1 δ	Mean	1 δ	Mean	1 δ	Mean	1 δ
Reference fossil diesel	0	1 200	45	0.4	6.7	0.137	739	15	34.84	0.45	6.6	0.069	740	15	34.50	0.59
n-octadecane	0	1 200	45	0.4	3.7	0.000	747	17	35.41	0.61	3.6	0.050	747	17	35.27	0.75
Methyl oleate	0	1 200	45	0.4	6.1	0.000	820	~	34.29	~	5.9	0.000	823	~	34.07	~
Methyl stearate	0	1 200	45	0.4	4.4	0.094	816	16	35.16	0.51	4.3	0.082	815	18	35.04	0.48
Ethyl stearate	0	1 200	45	0.4	4.3	~	804	~	35.31	~	4.3	~	801	~	34.68	~
n-propyl stearate	0	1 200	45	0.4	4.5	~	816	~	35.35	~	4.3	~	817	~	34.90	~
n-butyl stearate	0	1 200	45	0.4	4.5	~	843	~	34.90	~	4.4	~	848	~	34.26	~
iso-propyl stearate	0	1 200	45	0.4	4.5	0.000	847	31	35.26	0.15	4.4	0.100	864	44	34.96	0.46
iso-butyl stearate	0	1 200	45	0.4	4.5	~	820	~	35.53	~	4.3	~	829	~	34.88	~
tert-butyl stearate	0	1 200	45	0.4	4.9	~	862	~	34.82	~	4.7	~	854	~	34.54	~

Constant ignition delay timing experiments																
Reference fossil diesel	15 322	1 200	45	0.4	4.7	~	725	~	33.74	~	4.4	~	723	~	33.70	~
n-methyl oleate	11 338	1 200	45	0.4	4.5	~	804	~	34.58	~	4.4	~	805	~	34.23	~
n-methyl stearate	3 717	1 200	45	0.4	3.7	~	840	~	35.98	~	3.7	~	838	~	36.21	~
tert-butyl stearate	3 425	1 200	45	0.4	4.3	~	886	~	35.15	~	4.2	~	898	~	34.90	~

3. Results and discussion
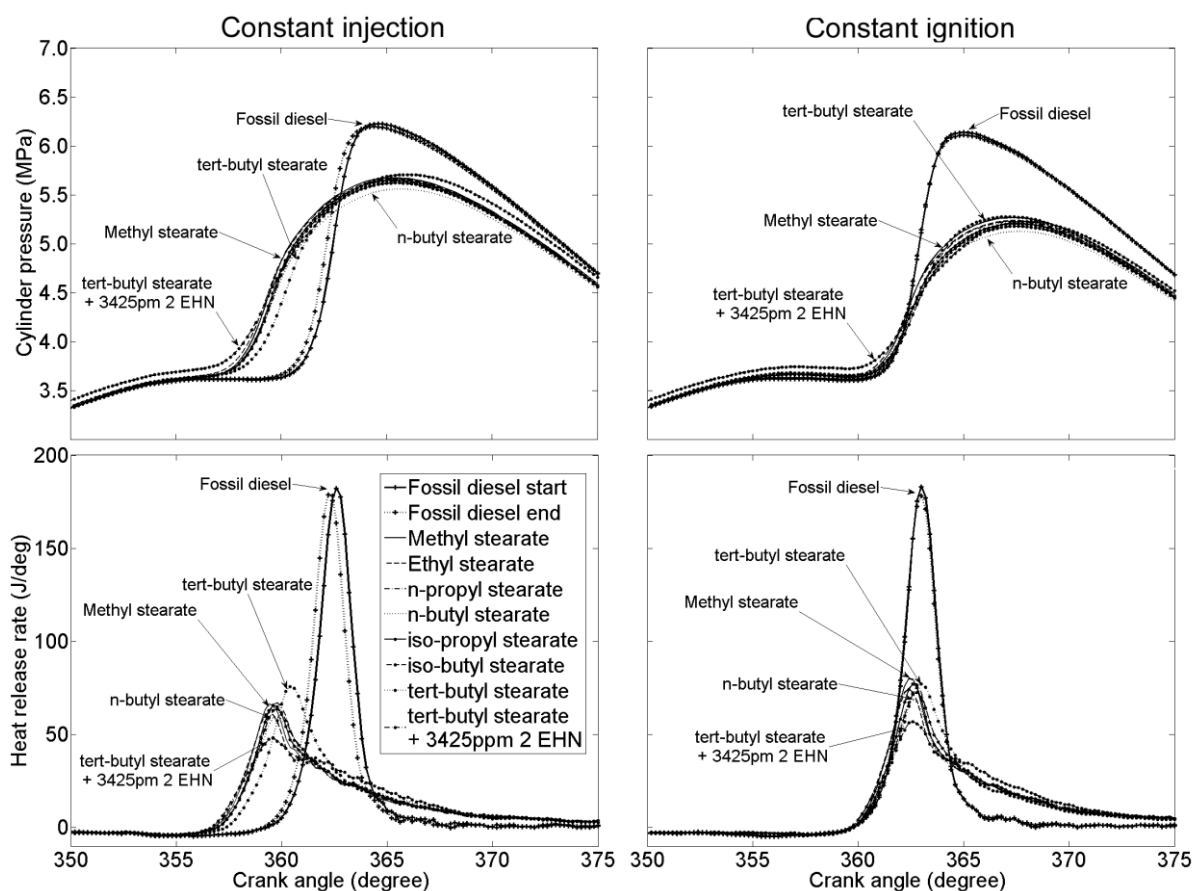
Figure 2. In-cylinder pressures and apparent net heat release rates of stearates and reference fossil diesel at constant injection and constant ignition timing.

All of the fatty acid esters in which the alcohol moiety was varied ignited after a shorter ignition delay than the reference fossil diesel, as shown in Figure 2. The esters also released a higher proportion of energy during diffusion combustion than the reference fossil diesel, resulting in a much longer duration of combustion (Figure 2). This is predominately attributable to the shorter ignition delay of the esters, which relative to the reference fossil fuel limits the extent of fuel and air premixing. Injection durations required for constant IMEP (Table 4) were also consistently longer for the fatty acid esters than the reference fossil diesel and this can be clearly attributed to the lower heating values of the esters (Table 2). Variation in the heat release rates of the fatty acid esters is apparent from Figure 2 and this is

16

discussed in the following sections, with respect to individual structural properties of the alcohol moiety.

3.1 Impact of the alcohol moiety straight carbon chain length
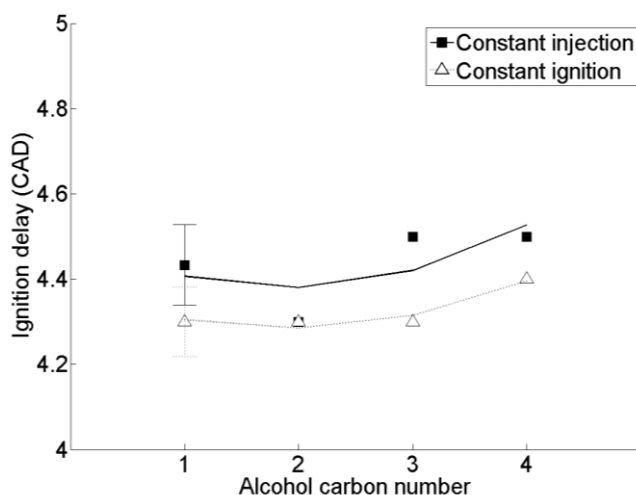

Figure 3. Influence of straight carbon chain length of the alcohol moiety in a fatty acid ester on ignition delay.

Figure 3 shows the impact of the alcohol moiety carbon chain length on the ignition delay at both constant injection and constant ignition timing conditions. It can be seen from Figure 3 that the variation found in ignition delay between the molecules of differing alcohol moiety carbon chain length (and also the day to day variation exhibited by n-methyl stearate) is equal, or less than, 0.2 CAD. As the shaft encoder utilized in measuring the in-cylinder pressure (from which the SOC, and thus ignition delay, was determined) has a resolution of 0.2 CAD, it is impossible from Figure 3 to discern an impact on ignition quality with varying alcohol moiety carbon chain length. The error bars presented in Figure 3 (plus and minus one standard deviation from the mean where repeat readings were taken; this definition is used consistently where error bars are presented in this paper) are around 0.2 CAD in total magnitude at both timing conditions suggesting that the largest source of experimental

17

uncertainty in determining the duration of ignition delay is indeed the shaft encoder resolution.

Previously, at the same experimental conditions, a very strong relationship was found between straight carbon chain length in n-alkanes and ignition delay[27]. As variation in the alcohol moiety carbon chain length has no discernable impact on the ignition delay, and for all the fatty acid esters tested the fatty acid moiety was a fully saturated straight carbon chain of length 18, it could be concluded that the ignition delay is being controlled solely by the fatty acid moiety. However, it is not possible to rule out a contribution in determining the duration of ignition delay from the alcohol moiety of the fatty acid ester. Figure 4[27] shows that for an n-alkane of carbon chain length C18, extension of the chain length to C20 and C22 has only a small influence on ignition delay which is not greater than the shaft encoder resolution of 0.2 CAD. If one considers the total carbon number of the fatty acid esters, then n-methyl stearate and n-butyl stearate have carbon numbers of 19 and 22 respectively. Therefore whilst clearly a gross oversimplification of the reaction kinetics involved, it is interesting to note that Figure 4 does suggest that the difference in ignition delay between these two molecules would be 0.2 CAD or less.

(In Figure 4 the form of the regression equation, $Y = Ax^b$, is used as it allows the exponent b to provide a measure of the impact x has on Y (e.g. ignition delay), because $\dfrac{\frac{dY}{Y}}{\frac{dx}{x}} = b$. This means that a 1% change in x will cause a b% change in Y, and so in Figure 4 for every 10% increase in the carbon length, the ignition delay reduces by 5%).

Figure 5 shows the effect on peak heat release rate of the alcohol moiety carbon chain length at both timing conditions; constant injection and constant ignition. While the trend generally apparent is for decreasing peak heat release rate with increasing alcohol moiety

carbon chain length, at both timing conditions n-propyl stearate produced a higher peak heat
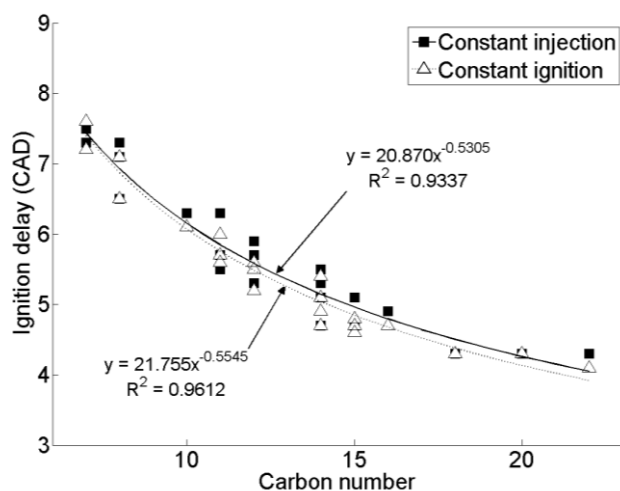
release rate than n-ethyl stearate.

Figure 4. Influence of straight carbon chain length on ignition delay in an n-alkane[27].
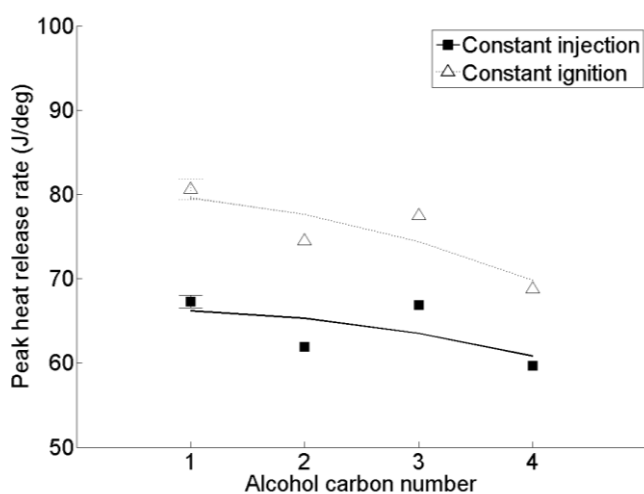

Figure 5. Effect of straight carbon chain length of the alcohol moiety in a fatty acid ester on

peak heat release rate.

   The range of error shown by the results in Figure 5 is smaller than the difference between

the maximum and minimum peak heat release rates recorded at both timing conditions,

suggesting that the non-linear trends observed do exist. It is suggested that the trends in peak

heat release can be attributed to differing premixed burn fractions, as the two have previously been found to correlate well[27] and it follows that greater peak heat release rates will be obtained when a greater proportion of fuel and air has been mixed to combustible stoichiometry prior to ignition. Two explanations for differing premixed burn fractions which could account for the trends seen in Figure 5 are offered, firstly that of an underlying trend in ignition delay. To test this theory, use was made of a previously found relationship between the ignition delay and peak heat release rate of acyclic non-oxygenated hydrocarbons[27]. At both constant injection and constant ignition timing, the shift in peak heat release rate corresponding to the uncertainty in measurement of the ignition delay of the fatty acid esters was calculated (the difference in peak heat release for a fuel of ignition delay 4.5 CAD and for a fuel of ignition delay 4.3 CAD) and found to be 7.1 J/deg and 6.7 J/deg for constant injection and constant ignition timing respectively. For both timing conditions these shifts are of roughly the same magnitude as the difference between the highest and lowest peak heat release rates exhibited by the fatty acid esters in Figure 5. This lends support to the hypothesis that differences in ignition delay of the fatty acid esters, beyond the resolution of the shaft encoder, account for the trends in peak heat release rate. Under this hypothesis methyl and n-propyl stearates possess the longest ignition delays (allowing more time for fuel and air mixing and thus a larger premixed burn fraction resulting in higher peak heat release rates), while n-butyl stearate exhibits the shortest ignition delay. This would a suggest a non-linear relationship between the carbon chain length of the alcohol moiety and the ignition quality of the fatty acid ester, as found in cetane measurements by Knothe et al.[19] The shorter ignition delay of the ethyl ester is also in agreement with the engine studies of Schönborn et al.[18] and Zhang et al.[24]. However, while there is some support in the literature for this theory, it must be highlighted that this hypothesis assumes that the relationship between ignition delay and peak heat release found in the study of acyclic non-oxygenated hydrocarbons

remains valid in the case of fatty acid esters. The second hypothesis offered to which the trends in Figure 5 can be attributed, is that a physical property of the esters, such as boiling point, may be sufficiently influential in determining the extent of fuel and air mixing during equivalent periods of ignition delay. However, the linear increase in boiling point with alcohol moiety chain length (Table 2) does not correlate well the non-linearity apparent in Figure 5.

Figure 6 shows a linear decrease in calculated maximum in-cylinder temperature with increasing alcohol moiety carbon chain length, therefore consistent with the peak in-cylinder pressures recorded (Figure 2). The non-linear relationship between alcohol moiety carbon chain length and peak heat release rate (Figure 5) is reflected in the timing of the calculated maximum in-cylinder global temperature (Figure 6), those esters which exhibited a higher peak release rate (Figure 5) reached the maximum in-cylinder temperature earlier.
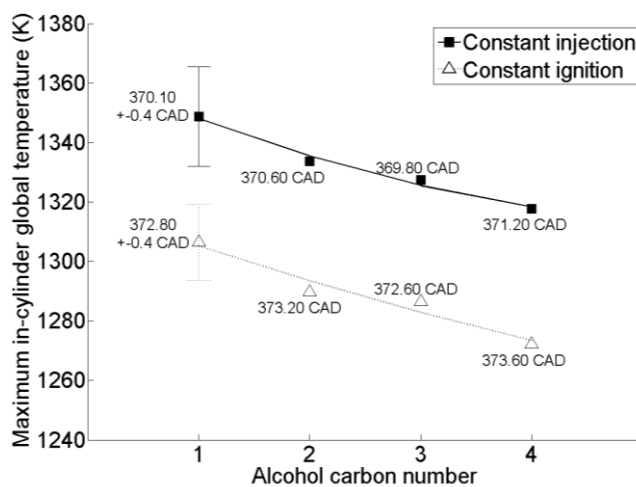

Figure 6. Impact of straight carbon chain length of the alcohol moiety in a fatty acid ester on calculated maximum global in-cylinder temperature and time of occurrence

Figure 7 shows the effect of alcohol moiety carbon chain length on the levels of NOx in the exhaust gas, at constant injection and constant ignition timing, and shows the methyl and butyl esters to emit the highest and lowest exhaust levels respectively. Formation of NOx in

the combustion of fatty acid esters has been suggested to be primarily by the thermal (Zeldovich) mechanism[44]. Both the global maximum in-cylinder temperature achieved and the time at which it is reached have been put forward as the primary driver of NOx formation and the ignition quality is fundamental in determining both of these variables[18,45,46]. Earlier and faster combustion events increase the duration for which in-cylinder conditions are suitable for NOx formation. Notwithstanding the error margins presented, a possible interpretation of the trend seen in Figure 7 is that both the timing and magnitude of the global maximum in-cylinder temperature are exerting an influence; in particular the non-linearity of the trend in Figure 7 may be attributable to the similarly non-linear timing of maximum in-cylinder global temperatures shown in Figure 6.
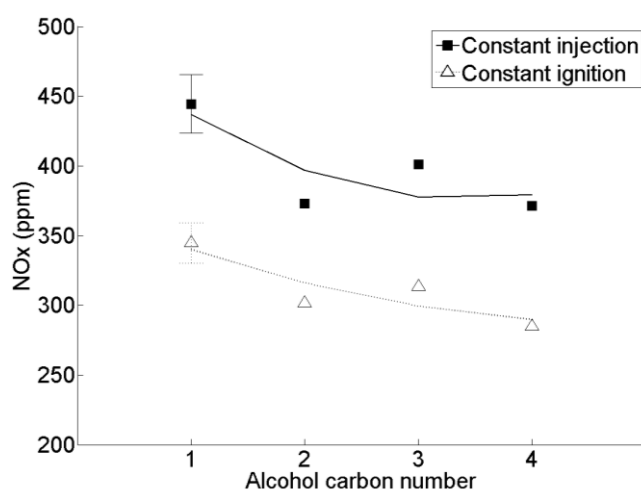

Figure 7. Impact of straight carbon chain length of the alcohol moiety in a fatty acid ester on NOx emissions.

Additionally, when calculating the shifts in NOx emissions that could be expected from the uncertainty in the ignition delay of the fatty acid esters (utilizing a previously found relationship between NOx emissions and ignition delay[27]), these are found to be less than the observed difference in the maximum and minimum NOx emissions from the fatty acid esters at both constant injection and constant ignition timing (significantly so for constant injection

timing where the calculated shift is 23 ppm and the difference between NOx emissions from n-methyl and n-butyl stearate is 56 ppm). Previously with the ignition delay of fuels equalized, the adiabatic flame temperature has been found to influence NOx formation[18,27].

For this reason, the adiabatic flame temperature at constant pressure was calculated, assuming no dissociation and an equivalence ratio of 1 using the method described by Turns[47] for the calculated minimum in-cylinder global temperature between SOI and SOC. The enthalpies of formation of all fuels except methyl stearate, ethyl stearate and n-octadecane were calculated from the lower heating values of the fuels obtained by the IP12 method[43] and shown in Table 2. In the case of methyl stearate and n-octadecane the lower heating values presented in Table 2 were calculated from the literature values of the enthalpies of formation in a liquid state[32,41]. The lower heating value of ethyl stearate is calculated from the enthalpy of formation in a solid state[32] and the enthalpy of fusion[33]. The results of the adiabatic flame temperature calculations are shown in Figure 8. In this case the adiabatic flame temperature does not appear to be a major contributor to the levels of NOx production, as the molecule with the highest adiabatic flame temperature (n-butyl stearate) exhibits the lowest level of exhaust gas NOx emissions. As the error bars present in Figure 8 are of some significance relative to the visible trend and are the result of deviation in the start temperature of the adiabatic flame temperature calculations, the same calculations were repeated for a constant starting temperature and the same trend with increasing alcohol moiety carbon chain length observed.

A further physical property of the esters which could account for the trend apparent in Figure 7 is that of oxygen content. As the alcohol moiety carbon chain length increases the percentage oxygen content of the stearates decreases. The effect of this decrease could have two important effects: to reduce the availability of oxygen for NOx formation and to decrease the level of mixture at stoichiometric conditions suitable for combustion at SOC, thus

resulting in lower peak heat release rates and maximum in-cylinder temperatures[46](though the latter seems unlikely given the non-linearity of the trends seen in Figure 5).
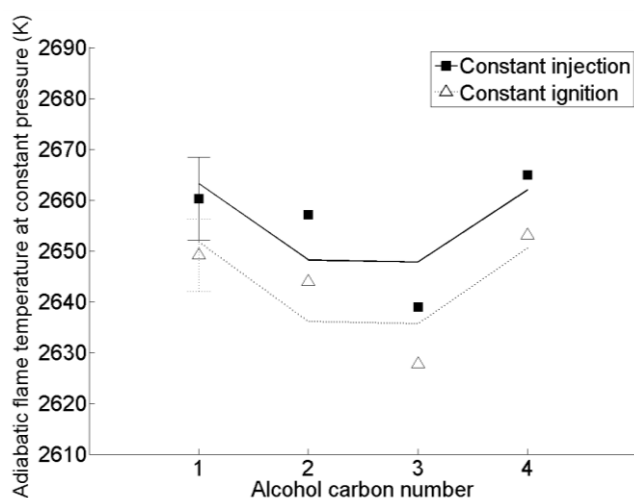

Figure 8. Impact of carbon chain length in the alcohol moiety on constant pressure adiabatic flame temperature.

Figure 9 shows the effect of alcohol moiety carbon chain length on exhaust gas emissions of CO, THC and the peak number of nucleation mode particles (those of diameter less than 50 nm). In the case of all three pollutants, the trend is for a peak in the emission level at an alcohol moiety carbon chain length of 2 or 3. However, the range of error for these emissions is high, especially in the case of THC. Therefore, while only very tentative inferences can be made from these results, there does appear to be a correlation between the levels of all three emissions at varying alcohol moiety carbon chain length. Both CO and THC are known products of incomplete combustion (a possible effect of both insufficient fuel and air mixing and over-dilution of fuel in air), and it has previously been suggested that a large proportion of nucleation mode particles are in fact droplets of un-burnt fuel[18].

Figure 10 shows a trend of increasing total mass of particulates measured in the exhaust gas with increasing alcohol moiety carbon chain length. From the molecules tested the trend appears exponential; at both timing conditions addition of a carbon atom to the straight

carbon chain of the alcohol moiety results in at least a doubling of the total mass of particulates produced. This trend appears to be a continuation of the result found by Schönborn et al.[18], where ethyl oleate was found to produce roughly double the mass of particulates of methyl oleate at constant ignition delay timing.
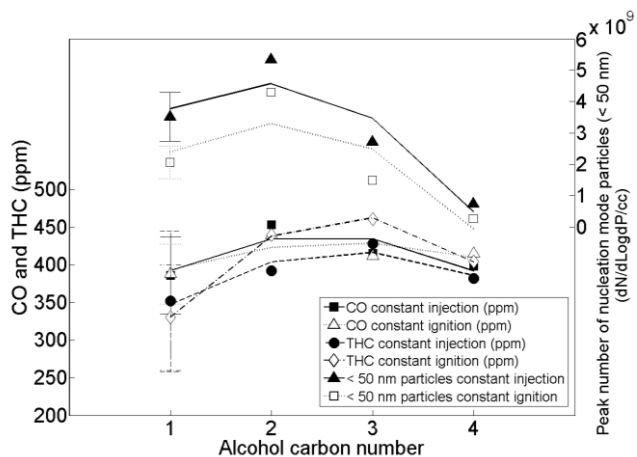

Figure 9. The influence of carbon chain length in the alcohol moiety on exhaust emissions of CO, THC and peak number of nucleation mode particles (< 50 nm).
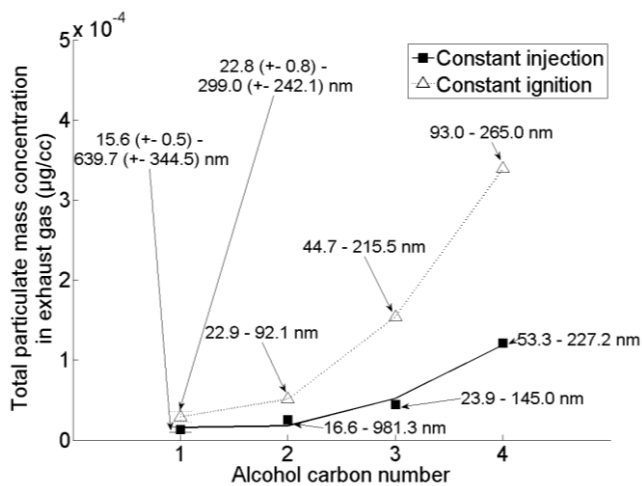

Figure 10. Impact of carbon chain length in the alcohol moiety on the total mass of particulates in the exhaust gas, including the particle diameter range in which 5 – 85 % of the total particulate mass is produced.

It is possible that the trends seen in Figure 10 are, at least in part, the effect of the trends in calculated maximum in-cylinder temperature seen in Figure 6. It is apparent that the ester producing the highest mass of particulates, n-butyl stearate, also experienced the coolest estimated global in-cylinder temperatures. Rates of soot oxidation are known to be thermally sensitive, with reactions rates increasing with temperature[48]. However, the strength of the trend would perhaps suggest that other factors are also of importance. Poorer fuel atomization could be expected to increase the presence of fuel rich zones which are conducive to the production of particulate matter[48]; the efficiency of fuel atomization is determined by a number of physical properties of the fuel, including boiling point. In Table 2 it can be seen that the boiling point of the fatty acid esters increases with alcohol moiety carbon chain length. Increased boiling points may reduce the efficiency of fuel atomization by increasing the energy required for fuel vaporisation, and so the trend in boiling point does correlate well with the trend seen in Figure 10. However, it must be iterated that values for the enthalpy of vaporisation are not available for the fatty acid esters and the correlation of boiling point with enthalpy of vaporisation is not guaranteed. Though a value of viscosity was not available for n-butyl stearate (Table 2), viscosity of the fatty acid esters does increase with alcohol moiety carbon chain length. This could also be expected reduce the efficiency of fuel and air mixing, with the fuel droplet size increasing with viscosity. An influence of increasing fuel melting point reducing the efficiency of fuel atomization (as postulated by Schönborn et al.[18]) is not apparent as it can be seen that fuel melting point (Table 2) actually decreases with increasing alcohol moiety carbon chain length and the total mass of particulates emitted. Another potential driver of the trend in Figure 10 is the decreasing oxygen content of the stearates with increasing alcohol moiety carbon chain length. This would decrease the availability of oxygen for soot oxidation after initial formation[48].

An influence of soot radiative heat transfer on the exhaust gas levels of NOx (Figure 7), which has previously been suggested as accounting for an increase in NOx emissions from fatty acid esters relative to those from fossil diesel[18,46], is possibly apparent when comparing Figure 7 with Figure 10. However, the non-linearity of the trend in Figure 7 is not reflected in Figure 10, nor is the exponential increase in particulate mass with increasing alcohol moiety carbon chain length (Figure 10) visible when inspecting Figure 7.

3.2 Effect of carbon chain branching in the alcohol moiety

In order to observe the impact on combustion and emissions of branching in the alcohol moiety of fatty acid esters, combustion characteristics and emissions levels have been plotted on the y axis as a shift relative to the value of the variable exhibited by the fatty acid ester with equivalent alcohol moiety straight carbon chain length. This shift is plotted against the ratio of branched carbon atoms present in the alcohol moiety relative to the straight carbon chain length in the alcohol moiety. For example, iso-propyl stearate has an alcohol moiety straight carbon chain length of 2 and one carbon present as a methyl branch in the alcohol moiety. Therefore the percentage branching of iso-propyl stearate is 50% and the y axis values plotted are shifts relative to ethyl stearate (which possesses the same straight alcohol moiety carbon chain length of 2).

Figure 11 shows the effect of carbon branching in the alcohol moiety on ignition delay. It can be seen that for iso-propyl stearate and iso-butyl stearate any shift (relative to n-ethyl stearate and n-propyl stearate respectively) is within the shaft encoder resolution of 0.2 CAD for both constant injection and constant ignition timing. However, the molecule with the highest degree of branching in the alcohol moiety, tert-butyl stearate does show a measurable increase in ignition delay (relative to n-ethyl stearate, and thus all the other stearates tested) at both timing conditions. A similar influence of branching on ignition delay has been observed

previously in the case of alkanes[27], where increasing the degree of branching resulted in a longer ignition delay.
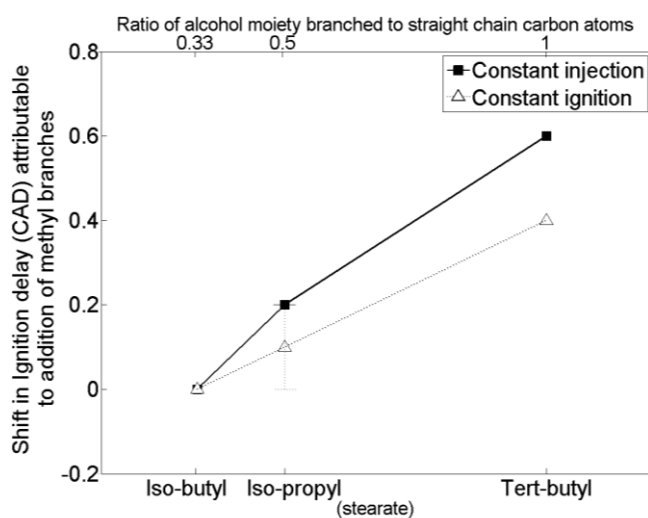

Figure 11. Influence of carbon chain branching in the alcohol moiety in a fatty acid ester on ignition delay.

With only one of the branched esters showing a change in ignition quality relative to the un-branched ester of equivalent alcohol moiety straight carbon chain length, the combustion and emissions characteristics of the branched esters are compared with ignition delay removed entirely as a variable. This was achieved by iteratively adding small quantities of the of the ignition promoting additive (2 EHN) to tert-butyl stearate until it exhibited the same duration of ignition delay (within the shaft encoder resolution) as the other stearates tested.

Figure 12 shows the effect of branching in the alcohol moiety on the peak heat release rate measured at constant ignition delay. The same general trend in results was obtained at both constant injection and constant ignition timing, with only tert-butyl stearate showing a decrease (~15 J/CAD) in peak heat release outside both the range of error and the variation that could be accounted for by the uncertainty in ignition delay due to the shaft encoder resolution (calculated according to the previously found relationship between peak heat release rate and ignition delay[27]).
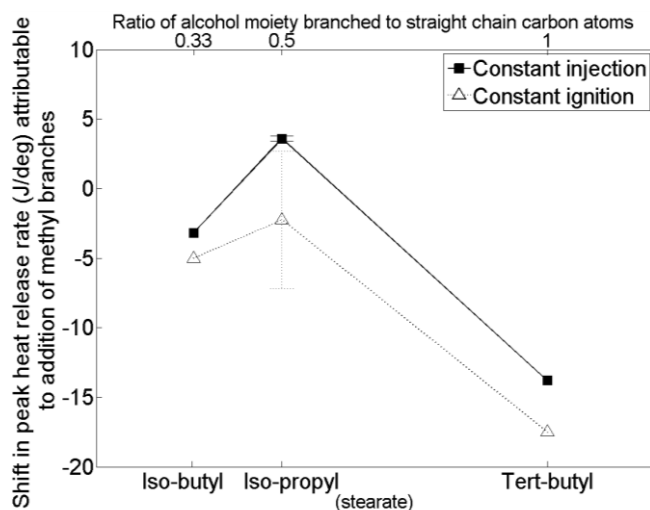
Figure 12. Influence of carbon chain branching in the alcohol moiety in a fatty acid ester on peak heat release rate at constant ignition delay.

From Figure 12 it can be seen that the addition of 2 EHN to tert-butyl stearate caused the fuel to switch from exhibiting the highest peak heat release rate of the stearates tested to the lowest (the former can be explained by a difference in ignition delay, the second cannot). As tert-butyl stearate is the only stearate to have been treated with 2 EHN, it is possible that the presence of the additive is affecting the peak heat release rate through mechanisms other than the change in ignition delay. The slightly higher peak heat release rate of iso-butyl palm ester relative to n-butyl palm ester (attributed to a slightly longer ignition delay) reported by Kinoshita et al.[25] is not apparent when considering the same esters of stearic acid.

Figure 13 shows a trend of increasingly large positive relative shifts in the calculated maximum in-cylinder global temperature with the increasing ratio of carbon atoms present as methyl branches in the alcohol moiety of a fatty acid ester, at both timing conditions. It also shows that for iso-butyl and iso-propyl stearate the timing of maximum in-cylinder temperature move later and earlier respectively in comparison to the esters of equivalent alcohol moiety straight carbon chain length. While the large margin of error presented makes it difficult to draw any firm conclusions from these results, it is interesting to note that tert-

butyl stearate shows a relative increase in maximum in-cylinder temperature despite a decrease in peak heat release rate (Figure 12). Decreasing peak heat release rates have previously coincided with decreasing maximum in-cylinder temperatures[27] and there is little shift in the timing of the maximum in-cylinder temperature (<= 0.2 CAD). Whether this shift in maximum in-cylinder temperature can be attributed to a property of the fuel or the presence of 2 EHN is uncertain.
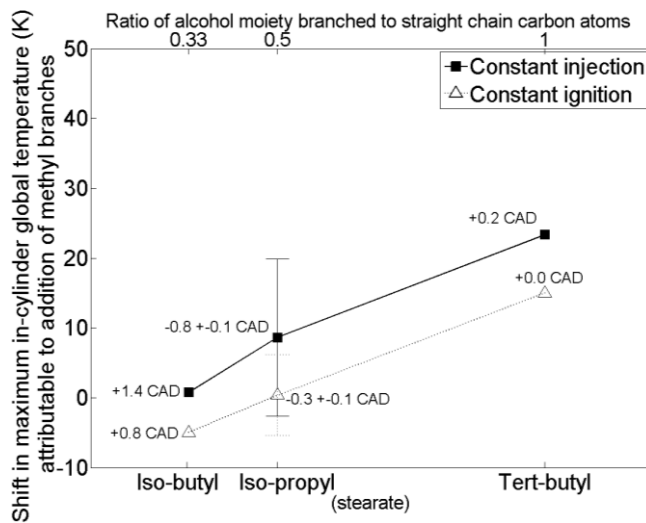

Figure 13- Effect of carbon chain branching in the alcohol moiety in a fatty acid ester on the calculated maximum in-cylinder global temperature and time of occurrence at constant ignition delay timings.

Figure 14 shows the impact of branching in the alcohol moiety on the levels of NOx exhaust emissions, at both constant ignition delay timings. The trend at both timing conditions is for an increasingly large shift in NOx levels relative to the equivalent un-branched fatty acid ester with increasing ratio of branched methyl groups present. When considering the thermally sensitive nature of NOx production, this is consistent with the trends in maximum in-cylinder global temperature seen in Figure 13.
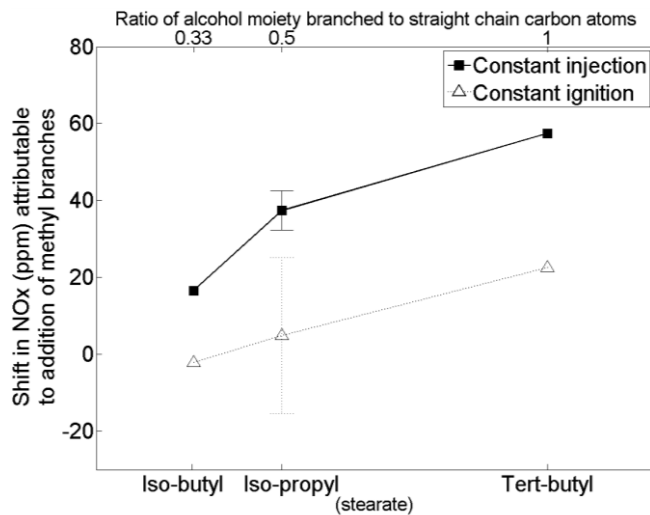
Figure 14. Influence of branching in the alcohol moiety on exhaust emissions of NOx at constant ignition delay timings.

Figure 15 shows the shift in the constant pressure adiabatic flame temperature attributable to the addition of methyl branches to the straight carbon chain in the alcohol moiety of the fatty acid esters. While all of the branched esters display a relative increase in adiabatic flame temperature, iso-butyl stearate displays a greater relative increase than iso-propyl stearate. This is not reflected in Figure 14 where iso-propyl stearate shows a greater relative increase in NOx emissions. Furthermore, the relative shifts in temperature are small (15 K) with a range of error equivalent in magnitude. Therefore, if the adiabatic flame temperature is an influence on NOx emissions it would appear to be secondary to the maximum in-cylinder global temperature (Figure 13).
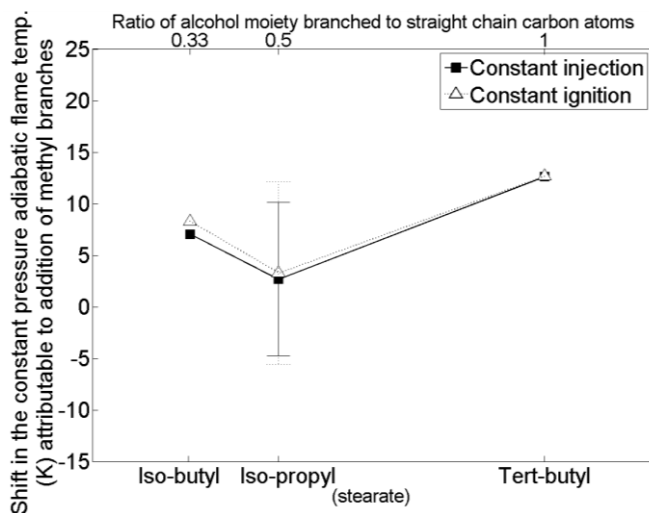
Figure 15. Impact of branching in the alcohol moiety on the constant pressure adiabatic flame temperature.

Figure 16 shows the effect of branching in the alcohol moiety of a fatty acid ester on exhaust gas emissions of CO, THC and the peak number of nucleation mode particles. At both timing conditions, the addition of branches appears to reduce CO levels, especially in the case of iso-propyl stearate. Emissions of THC are reduced by as much as 100 ppm by the addition of branches, apart from in the case of tert-butyl stearate in which they are increased by a similar amount. However, when considering the trends in both CO and THC it must be noted that the range of the results is roughly equal to the range of error under both timing conditions.

Figure 16 does, however, show results for peak number of nucleation mode particles that are significantly outside of the experimental variability and which are also outside of the range of error brought about by uncertainty in the ignition delay (as calculated from a previously determined relationship between peak number of nucleation mode particles and ignition delay[27]). The addition of a methyl branch to the alcohol moiety of n-propyl stearate (to form iso-butyl stearate) increases the number of nucleation mode particles, while making the same addition to ethyl stearate (to form iso-propyl stearate) results in a drop in the

number of nucleation mode particles. At constant injection constant ignition delay timing tert-butyl stearate shows a small relative decrease in the peak number of nucleation mode particles, but at constant ignition constant ignition delay timing a larger increase in the peak number of nucleation mode particles.
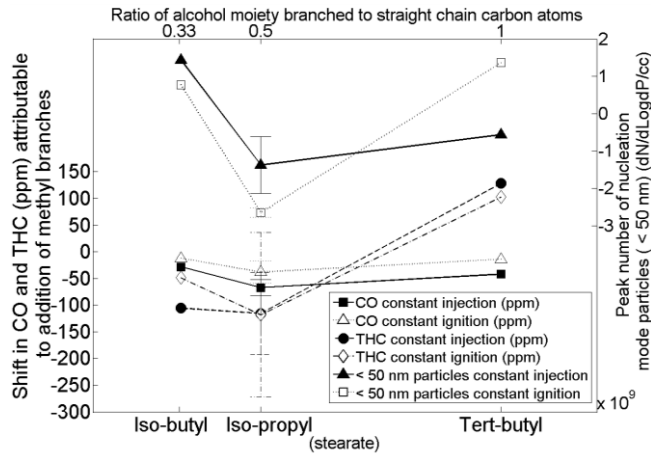

Figure 16. The influence of branching in the alcohol moiety on exhaust emissions of CO, THC and peak number of nucleation mode particles (< 50 nm) at constant ignition delay timings.

Shown in Figure 17 is the effect of branching in the alcohol moiety on the total mass of particulates produced at both constant ignition delay timings. At constant injection constant ignition delay timing, iso-butyl stearate shows a slight decrease in the total mass of particulates produced relative to the un-branched fatty acid ester of equivalent alcohol moiety straight carbon chain length. Iso-propyl stearate shows little shift in the total mass of particulates, while the most branched molecule, tert-butyl stearate, shows an increase in the total mass of particulates produced. The same general trend is apparent in the results of tests conducted at constant ignition constant ignition delay timing, though the magnitude of the shifts seen is significantly greater and with iso-propyl stearate displaying a relative increase in the total mass of particulates produced. At both constant injection and constant ignition timing the measured day-to-day variability is smaller than the range of results. Revisiting the

theories put forward when considering the effect of alcohol moiety carbon chain length on total particulate mass (Figure 10), an effect of temperature seems unlikely as the molecule displaying the largest increase in particulate mass also an increase in maximum in-cylinder global temperatures.
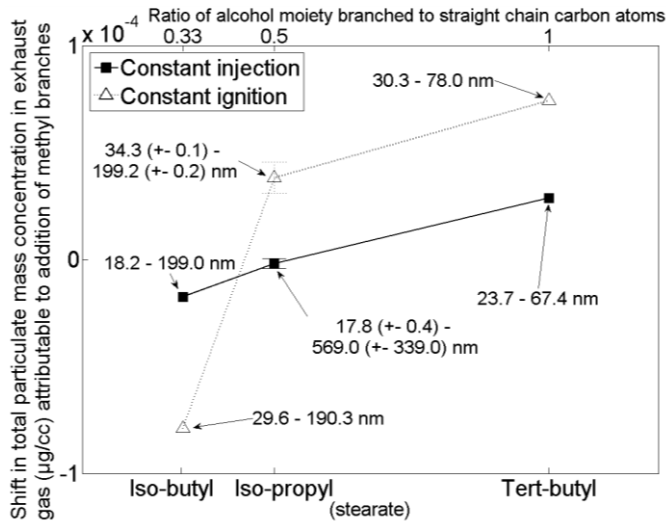

Figure 17. The effect of branching in the alcohol moiety on the total mass of particulates in exhaust emissions with ignition delay removed as a variable, including the particle diameter range (absolute) in which 5 – 85 % of the total particulate mass is produced.

When comparing Figure 17 to Figure 10, it can be seen that in Figure 10, at both timing conditions, the addition of two carbon atoms to the straight chain length of the alcohol moiety of n-ethyl stearate to form n-butyl stearate results in a larger increase in the total mass of particulates produced than the addition of two methyl branches to form tert-butyl stearate (Figure 17). Studies have found that sooting tendencies tend to increase with both increasing straight carbon chain length and the addition of methyl branches[49].

3.3 Importance of the alcohol moiety relative to other structural properties of fatty acid esters

Previous studies have looked at extensively at the impact of structural features other than the alcohol moiety of fatty acid esters on combustion and emissions, notably the degree of unsaturation, carbon chain length of the fatty acid moiety and also the presence of the ester functional group through comparison to normal alkanes[18,19,23,24,46,50-52]. To gauge the importance of alcohol moiety structure on the combustion and emissions of fatty acid esters relative to these better understood structural properties a further series of experiments were conducted at constant injection, constant ignition and constant ignition delay timings. In these the combustion characteristics and exhaust emissions levels of n-methyl stearate were compared to n-methyl oleate, n-octadecane and a reference fossil diesel with zero fatty acid ester content.

Figure 18 shows that the properties of alcohol moiety structure found are, at both constant injection and constant ignition timing, of less significance in determining the duration of ignition delay than the fatty acid moiety degree of saturation and roughly equivalent to the importance of the presence of the ester functional group. The ignition delays exhibited by methyl oleate, n-octadecane and the reference diesel relative to methyl stearate are consistent with previous studies [18,24].
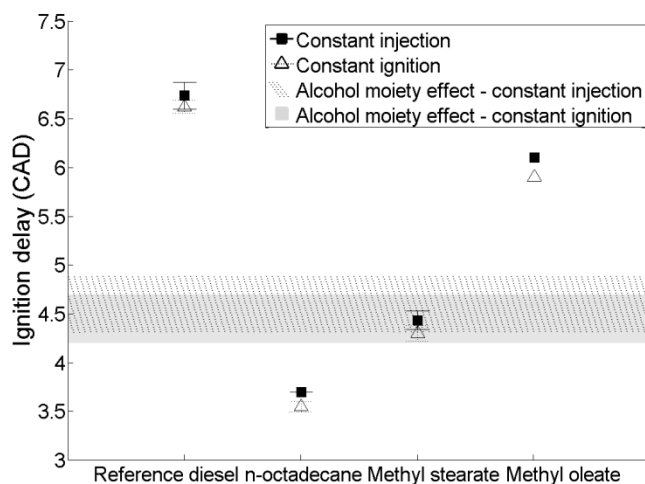
Figure 18. Ignition delay of reference fuels and impact of the alcohol moiety at constant injection and constant ignition timing.

Figures 19 – 22 compare the impact of the alcohol moiety with the other features of fatty acid ester molecular structure at constant ignition delay timings. As before, this was achieved by iteratively adding small quantities of the of the ignition promoting additive (2 EHN) until the fuel exhibited the desired ignition delay. Equalizing the delays of all four fuels was not practical due to the large spread observed in the delays; neither was it desirable as 2 EHN contains fuel bound nitrogen and oxygen which may contribute to total NOx emissions. Therefore, the reference fossil diesel and n-methyl oleate were equalized to the same ignition delay as that of n-methyl stearate, and then separately, n-methyl stearate was equalized to the same ignition delay as that of n-octadecane. This was done at both constant injection and constant ignition timings, and as such the results are presented as two sets of data acquired at two equalized values of ignition delay for each timing condition.

Figure 19 shows the peak heat release rates recorded for each of the fuels at constant injection and constant ignition constant ignition delay timing. It can be seen that alterations to the structure of the alcohol moiety are of far greater significance in determining rates of peak heat release than introducing a single double bond to the fatty acid moiety, with no

36

discernable difference in the peak heat release rates of methyl stearate and methyl oleate. N-octadecane was found to possess a higher peak release rate than methyl stearate, but the range of variation brought about by the changes in the alcohol moiety is approximately twice this increase.
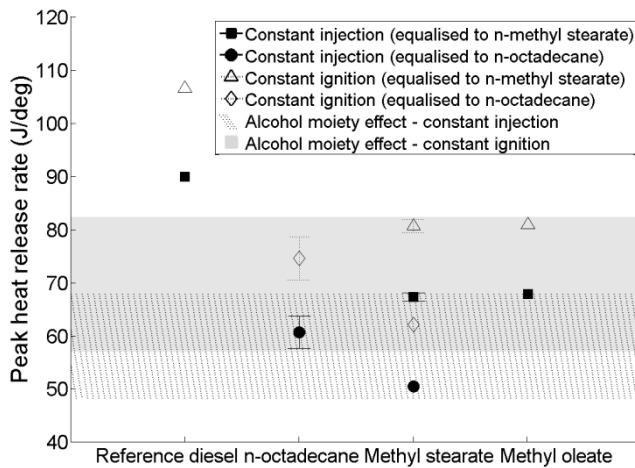

Figure 19. Peak heat release rate reference fuels and impact of the alcohol moiety at constant injection and constant ignition constant ignition delay timing.

Figure 20 shows the exhaust gas levels of NOx for each fuel and the variation brought about by changes to the alcohol moiety, at both constant injection and constant ignition constant ignition delay timing. From Figure 20 it can be seen that variation of the alcohol moiety (the most influential being the increase in alcohol moiety chain length, Figure 7) has approximately twice the impact on NOx emissions as the change in saturation from methyl stearate to methyl oleate, at both timing conditions. The observed increase in NOx emissions with the addition of a double bond (methyl stearate to methyl oleate) can be attributed to an increase in adiabatic flame temperature and is in agreement with the previous investigation into the effect of saturation in acyclic chain[27] and also the experimental findings of Schönborn et al.[18].
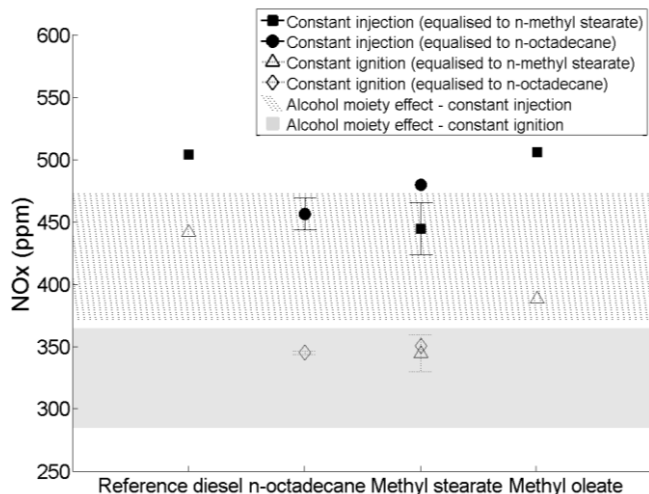
Figure 20. NOx emission levels of reference fuels and impact of the alcohol moiety at constant injection and constant ignition constant ignition delay timing.
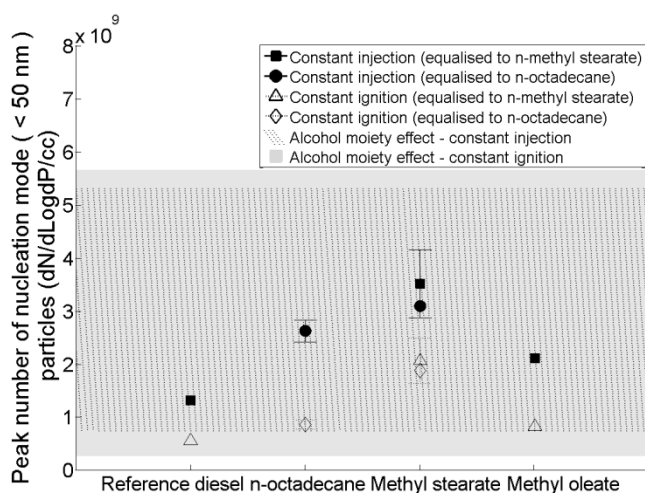

Figure 21. Peak number of nucleation mode particles (< 50 nm) of reference fuels and impact of alcohol moiety at constant injection and constant ignition constant ignition delay timing.

In Figures 21 and 22 the significance of the alcohol moiety structure in the production of nucleation mode particle and the total mass of particulates is presented. While Figure 21 does show alcohol moiety structure to be a larger influence on the peak number of nucleation mode particles than either the degree of fatty acid saturation or the presence of the ester functional group, far more striking is the impact of the alcohol moiety on the total particulate

mass produced. In Figure 22 it can be seen that the variation with alcohol moiety in the total mass of particulates produced dwarfs the effect of either fatty acid saturation or ester functional group, and that of the many differences between the reference diesel and the three pure component fuels tested alongside it.
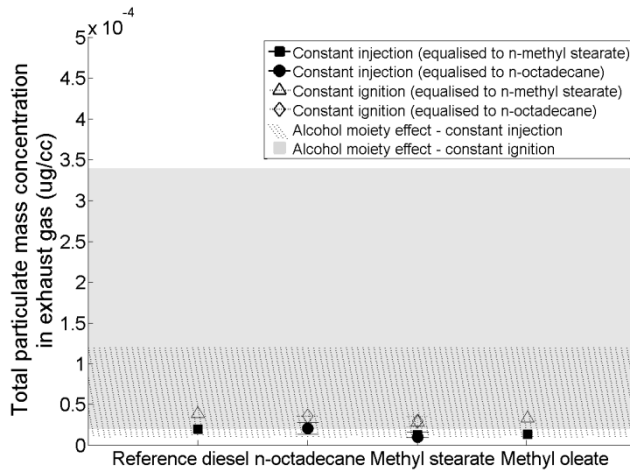

Figure 22. Total particulate mass concentration of reference fuels and the impact of the alcohol moiety at constant injection and constant ignition constant ignition delay timing.

3.4 Effect of injection timing

Visible in many of the engine experiment results is a clear offset between those taken at constant injection timing and those taken at constant ignition timing. For example, when considering the effect of carbon chain length in the alcohol moiety, Figure 5 shows that at constant ignition timing all fuels displayed a higher peak heat release rate than at constant injection timing. This is likely attributable to differences in physical conditions within the engine cylinder during fuel injection. As all fuels possessed an ignition delay of less than 7.5 CAD, when injection timing was adjusted for SOC at TDC (constant ignition timing) the SOI of every fuel was less than 7.5 CAD. It is suggested that the smaller cylinder volume and higher temperatures thus experienced during the fuel injection increased the level of fuel and

39

air mixing. Therefore, a greater amount of fuel and air was mixed to an ignitable equivalence ratio at SOC and a greater peak heat release rate resulted.
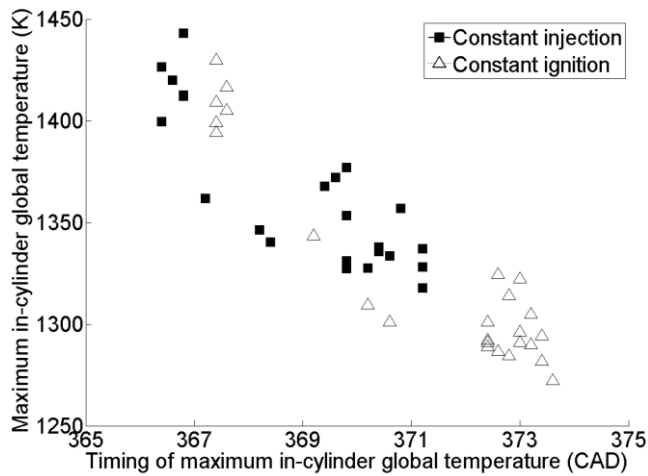

Figure 23.   Calculated maximum in-cylinder global temperature versus the timing of calculated maximum in-cylinder temperature for all fuels.

In Figure 6, it can be seen that despite producing higher peak heat release rates, experiments conducted at constant injection timing resulted in lower global maximum in-cylinder temperatures. At constant ignition timing, SOC commences later than at constant injection timing and so the maximum in-cylinder temperature also occurs later into the expansion stroke and thus at greater in-cylinder volumes, this is illustrated by Figure 23. The offset between levels of NOx and also the total mass of particulates at the two timings (Figures 7 and 10) is therefore clearly the result of the offset seen in Figure 6. It is also possible that these results are highlighting the importance of residence time of gases at elevated temperatures in the production of thermal NOx, as was suggested by Szybist et al.[53]

The same effects of injection timing are also readily apparent when considering the effect of the fatty acid functional group and the degree of saturation in the fatty acid moiety. At constant ignition timing, relative to measurements at constant injection timing, peak heat release rates are higher (Figure 19), while the global maximum in-cylinder temperatures are

40

lower, as are NOx emissions (Figure 20), and the total mass of particulates is increased (Figure 22).

3.5 Effect of molecular structure on adiabatic flame temperature

In the case of increasing carbon chain length in the alcohol moiety, it is hard to discern a firm trend in the adiabatic flame temperatures calculated (Figure 8). However, it can be seen that n-butyl stearate does possess a significantly higher adiabatic flame temperature than the other n-alkyl esters. This is also apparent when considering the lower heating value (Table 2) of the n-butyl stearate relative to the other n-alkyl esters. Increased carbon chain length could be expected to increase the adiabatic flame temperature as the carbon to hydrogen ratio decreases, but the reduced percentage oxygen content of n-butyl stearate might also be expected to decrease the adiabatic flame temperature. Considering the branched esters, the two with the highest degree of branching (iso-propyl stearate and tert-butyl stearate) showed an increase in adiabatic flame temperature relative to the esters of equivalent alcohol moiety straight carbon chain length. So as to investigate this further preliminary thermo-gravimetric analysis of some of the esters was undertaken. The two n-alkyl stearates tested (n-methyl and n-butyl stearate) showed one distinct mass loss event, potentially representative of a boiling point, while tert-butyl stearate displayed several mass loss events below the expected boiling point (Figure 24).
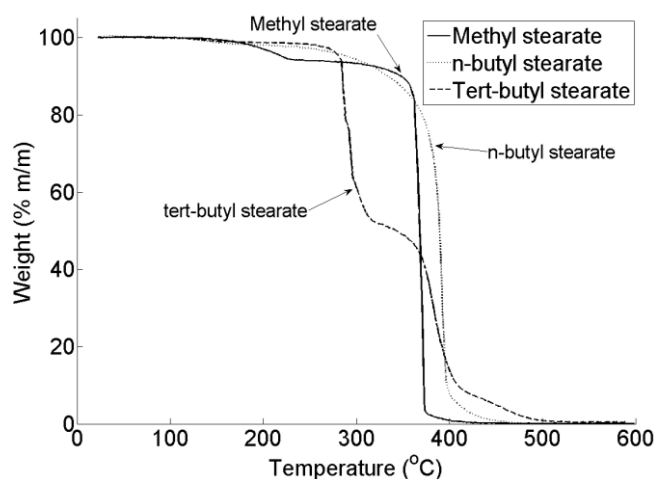
Figure 24. Thermo-gravimetric analysis of methyl, n-butyl and tert-butyl stearate.

Emran et al.[54] obtained similar results with TGA of tert-butyl ester terminated dendrimers. They find that the magnitude and occurrence temperature of the mass loss events closely correlate with the theoretical amounts of iso-butylene that would be produced were the tert-butyl moiety to separate from the ester moiety. It is therefore suggested that tert-butyl stearate is experiencing the same process of thermal decomposition prior to fuel vaporisation, with the production of isobutylene and the resulting carboxylic acid (stearic). A recent shock tube and kinetic modeling study[55] of methyl tert-butyl ether and ethyl tert-butyl ether found these species to undergo a similar thermal decomposition, with the high temperature reactivity of the ethers inhibited by the formation of iso-butene.

This could explain the decreased ignition quality of tert-butyl stearate relative to the other stearates tested. Cetane number measurements of tert-butyl stearate are not available, but iso-butyl stearate has been reported to possess a cetane number of near 99.3, while stearic acid was found to have a cetane number of 61.7[29]. Iso-butylene could also be expected to be of poor ignition quality too; the molecule is relatively short and the presence of a double bond and methyl branches have previously been found to further impair ignition quality[27].

It is also tentatively suggested that the thermal decomposition of tert-butyl stearate is responsible for an elevated adiabatic flame temperature relative to the ester of equivalent alcohol moiety straight carbon chain length. An increase in adiabatic flame temperature is known to occur when introducing a double bond and has been previously observed to be of sufficient importance to influence emissions formation when differences in ignition delay are not present[18,27]. Therefore, it is possible that the formation of iso-butylene and thus the addition of a further double bond to the reactant mix is having a similar effect. Though purely a speculative suggestion, it could also be that that the thermal degradation of tert-butyl stearate is responsible for the discrepancy between Figures 12 and 13 (tert-butyl stearate shows a decrease in peak heat release rate but an increase in in-cylinder maximum temperature).

From the TGA thus conducted it is not possible to draw any firm conclusions as to whether any of the other esters tested are experiencing similar thermal degradation. However, it is apparent that the single mass loss event experienced by n-methyl stearate is of much steeper gradient than that experienced by n-butyl stearate. One could therefore speculate that n-butyl stearate may be undergoing thermal degradation prior to vaporisation (though of a much lesser extent than tert-butyl stearate) and the resulting structure, perhaps with an increased number of double bonds, is responsible for the elevated adiabatic flame temperature seen in Figure 10. This could be an observation of the six centered uni-molecular elimination reaction suggested by Zhang et al.[23] It could also be that such a thermally induced change to the molecular structure is contributing to the increased levels of particulate mass for n-butyl stearate seen in Figure 10 (as some structural features, such as double bonds, are known to increase sooting levels[49]).

3.6 Effect of fuel physical properties

When in Section 3.1 considering the effect of fatty acid ester alcohol moiety carbon chain length on the total mass of particulates in the exhaust gas (Figure 10), it was suggested that a physical property of the esters maybe influencing the fuel atomization and thus levels of soot formation. Therefore, to investigate this hypothesis further Figure 25 shows the influence of fuel normal boiling point on the total mass of particulates produced in the exhaust gas for all the stearates tested at constant ignition delay timings. It can be seen that there is a degree of correlation between boiling point and particulate mass and that the one notable exception to the trend is tert-butyl stearate (boiling point 622.5 K). If the theory outlined in Section 3.5 that tert-butyl stearate is undergoing severe thermal degradation on injection and prior to soot formation is correct then it is not particularly surprising. However, it must be noted when considering the degree of correlation present in Figure 25 that the values of boiling point plotted are values calculated by a group theory method, not experimental data. The possible influence of other fuel physical properties, such as viscosity or enthalpy of vaporisation, for which experimental data is not readily available but which are likely to correlate well with boiling point must also not be overlooked.
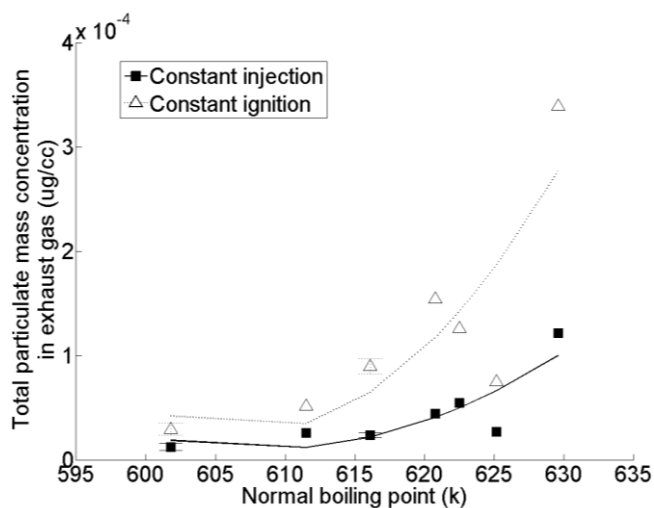
Figure 25. Effect of stearate normal boiling point on total mass of particulates in the exhaust gas at constant ignition delay timings.

3.7 Effect of fuel oxygen content

In section 3.1, when considering the effect of alcohol moiety carbon chain length, oxygen content of the stearates was mooted as a possible influence on emissions of NOx and particulate mass in the exhaust gas (Figures 7 and 10). Therefore Figures 26 and 27 show for all stearates tested, at constant ignition delay timings, the effect of oxygen on the exhaust gas emissions of NOx and particulate mass respectively. No significant correlation between oxygen content and NOx emissions can be seen in Figure 26, with branching in the alcohol moiety producing differing NOx levels even in the case of identical oxygen contents. Similarly, Figure 27 shows molecules of identical oxygen content to exhibit varying levels of soot production. In fact, as the degree of correlation in Figure 27 is somewhat less than that of Figure 25 (where the effect of stearate boiling point on particulate emissions was considered), it could be surmised that while an effect of fuel oxygen content cannot be entirely dismissed it is of less importance than the fuel boiling point (or correlated thermal property) in determining the levels of particulate mass produced.
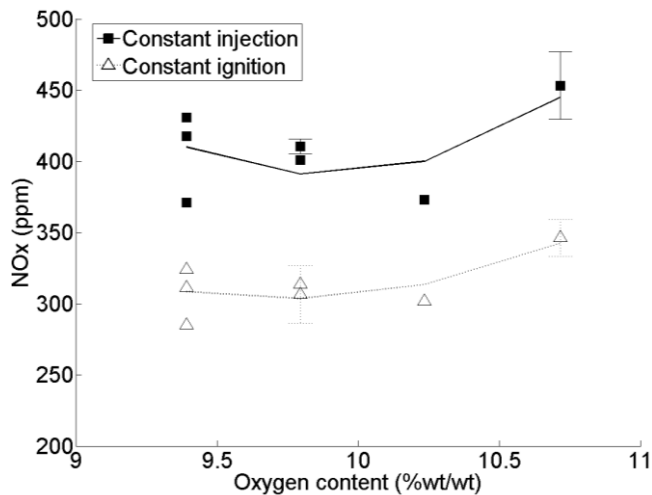
Figure 26. The influence of stearate oxygen content on exhaust gas emissions of NOx at constant ignition delay timings.
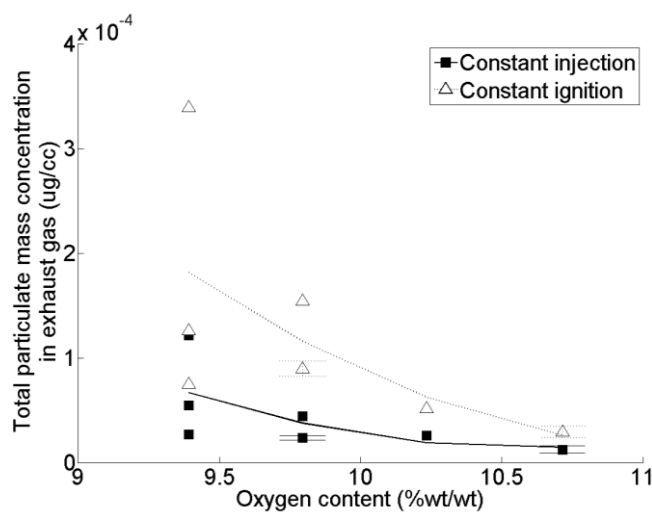

Figure 27. The impact of stearate oxygen content on total mass of particulates in the exhaust gas at constant ignition delay timings.

4. Conclusions

1. In esters of stearic acid, considering the alcohol moiety, an increase in the straight carbon chain length or the addition of methyl branches has no significant impact on the ignition quality of the fuel. Only addition of two methyl branches to the alcohol moiety of a fatty acid

46

ester resulted in a discernable, though slight, increase in ignition delay. Therefore, it would be possible to substitute fatty acid methyl esters with those of longer straight, or branched, alcohols without changes to the diesel combustion strategy.

2. With ignition delay completely removed as a variable, emissions of NOx reduce with the addition of carbon atoms to the alcohol moiety straight chain carbon length, but increase with the addition of methyl branches to the alcohol moiety. Such changes to the alcohol moiety are at least as significant in determining exhaust gas levels of NOx as the addition of one double bond to the fatty acid moiety of an ester.

3. The total mass of particulates in the exhaust gas increases with a longer alcohol moiety carbon chain and to a lesser extent the addition of methyl branches to the alcohol moiety. Both alcohol moiety carbon chain length and branching is of greater importance than the addition of one double bond to the fatty acid moiety or the presence of the ester functional in determining exhaust gas levels of particulate mass.

4. Even with little or no variation in ignition delay between fuels, the primary route by which levels of exhaust NOx are influenced by molecular structure is through estimated global maximum in-cylinder temperature. NOx levels decrease with decreasing maximum in-cylinder temperature which is a function of the peak heat release rate of a fuel and the combustion strategy.

5. Tert-butyl esters are known to thermally decompose prior to vaporisation. The products of this decomposition are expected to be of lower ignition quality than the original ester and would thus explain the observed increase in ignition delay of tert-butyl stearate relative to the other stearates.

In addition, one can advance the following hypotheses:

(a) A trend of ignition delay varying with alcohol carbon number can be deduced from the observed peak heat release rates and does not appear to be wholly attributable to experimental

variability. Increasing the alcohol moiety carbon chain length reduces ignition delay, though the trend is non-linear with n-propyl stearate possessing a slightly longer ignition delay than ethyl stearate.

(b) The thermal decomposition of tert-butyl stearate may also account for an observed increase in adiabatic flame temperature by increasing the number of double bonds present in the reactants. It is also possible that n-butyl stearate is undergoing thermal decomposition (although to a lesser extent) and impacting on the production of particulate mass.

(c) A physical property of the stearates, such as boiling point or viscosity, is a primary driver of soot production through influencing fuel atomization and subsequent fuel and air mixing.

(d) An effect of ester oxygen content on NOx and particulate emissions is possible but is certainly of less importance than the in-cylinder maximum global temperature in the case of NOx production. Considering soot production, it is likely to be at the highest of tertiary importance with in-cylinder maximum global temperatures and ester physical properties of more significance.

5. Acknowledgements

Nomenclature

FAME – Fatty acid methyl ester

NOx – Nitrous oxides

CO_2 – Carbon dioxide

IBE – Iso-propanol, butanol and ethanol

ABE – Acetone, butanol and ethanol

IQT – Ignition quality testing

BCN – Blended cetane number

RME – Rapeseed methyl ester

REE – Rapeseed ethyl ester

CO – Carbon monoxide

CFR – Cooperative Fuels Research

THC – Total hydrocarbons

CAD – Crank angle degree

PID - Proportional integral derivative

DAQ – Data acquisition

O_2 - Oxygen

SOI – Start of injection

BTDC – Before top-dead-centre

TDC – Top-dead-centre

SOC – Start of combustion

2 EHN – 2 ethyl hexyl nitrate

IMEP – Indicated mean effective pressure

PPM – Parts per million

TGA – Thermo-gravimetric analysis

References

(1)   Bach, W. *Environment International* **1979,** *2,* 215-228.

(2)   Wuebbles, D. J.; Jain, A. K. *Fuel Processing Technology* **2001,** *71,* 99-119.

(3)   Dooley, J. J.; Dahowski, R. T.; Davidson, C. L. *International Journal of Greenhouse Gas Control* **2009,** *3,* 720-730.

(4)   Zecca, A.; Chiari, L. *Energy Policy* **2010,** *38,* 1-3.

(5)   Hitz, S.; Smith, J. *Global Environmental Change Part A* **2004,** *14,* 201-218.

(6)   Badr, O.; Probert, S. D. *Applied Energy* **1993,** *44,* 197-231.

(7)   De Nevers, N. *Air pollution control engineering;* McGraw-Hill, Inc.: 1995.

(8)   European Union. Euro 5 and Euro 6 standards: reduction of pollutant emissions from light vehicles. 13-12-2010.
    Ref Type: Online Source

(9)   Ogden, J. M.; Steinbugler, M. M.; Kreutz, T. G. *Journal of Power Sources* **1999,** *79,* 143-168.

(10)   Rosillo-Calle, F.; Walter, A. *Energy for Sustainable Development* **2006,** *10,* 20-32.

(11)   Krouwel, P. G.; Groot, W. J.; Kossen, N. W. F.; van der Laan, W. F. M. *Enzyme and Microbial Technology* **1983,** *5,* 46-54.

(12)   Ezeji, T. C.; Qureshi, N.; Blaschek, H. P. *Current Opinion in Biotechnology* **2007,** *18,* 220-227.

(13)   www.gevo.com. 3-11-2011.
    Ref Type: Online Source

(14)   www.butamax.com. 3-11-2011.
    Ref Type: Online Source

(15)   Graboski, M. S.; McCormick, R. L. *Progress in Energy and Combustion Science* **1998,** *24,* 125-164.

(16)   Geuens, J.; Kremsner, J. M.; Nebel, B. A.; Schober, S.; Dommisse, R. A.; Mittelbach, M.; Tavernier, S.; Kappe, C. O.; Maes, B. U. W. *Energy Fuels* **2008,** *22,* 643-645.

(17)   Wahlen, B. D.; Barney, B. M.; Seefeldt, L. C. *Energy Fuels* **2008,** *22,* 4223-4228.

(18)   Schönborn, A.; Ladommatos, N.; Williams, J.; Allan, R.; Rogerson, J. *Combustion and Flame* **2009,** *156,* 1396-1412.

(19)   Knothe, G.; Bagby, M.; Ryan, T. W. *SAE Technical Paper Series* **1997**.

(20)   Serdari, A.; Lois, E.; Stournas, S. *Ind. Eng. Chem. Res.* **1999,** *38,* 3543-3548.

(21)   Makareviciene, V.; Janulis, P. *Renewable Energy* **2003,** *28,* 2395-2403.

(22)   Lapuerta, M. n.; Herreros, J. M.; Lyons, L. L.; Garc+¡a-Contreras, R.; Brice+¦o, Y. *Fuel* **2008,** *87,* 3161-3169.

(23)   Zhang, Y.; Yang, Y.; Boehman, A. L. *Combustion and Flame* **2009,** *156,* 1202-1213.

(24)   Zhang, Y.; Boehman, A. L. *Combustion and Flame* **2010,** *157,* 546-555.

(25)   Kinoshita, E. *JSAE Powertrains, Fuels and Lubricants Meeting* **2011,** 460-466.

(26)   Knothe, G.; Matheaus, A. C.; Ryan, T. W. *Fuel* **2003,** *82,* 971-975.

(27)   Hellier, P.; Ladommatos, N.; Allan, R.; Payne, M.; Rogerson, J. *JSAE 2011 Powertrains, Fuels and Lubricants Meeting* **2011,** 2011-01-1922.

(28)   Schönborn, A.; Ladommatos, N.; Williams, J.; Allan, R.; Rogerson, J. *SAE Technical Paper Series* **2007,** 2007-24-0125.

(29)   Murphy, M. J.; Taylor, J. D.; McCormick, R. L. *NREL/SR 540-36805* **2004**.

(30)   Knothe *Journal of the American Oil Chemists' Society* **2009,** *86,* 843.

(31)   Pratas, M. J.; Freitas, S.; Oliveira, M. B.; Monteiro, S. ü. C.; Lima, A. S.; Coutinho, J. â. A. P. *J. Chem. Eng. Data* **2010,** *55,* 3983-3990.

(32)   Maksimuk, Y.; Antonova, Z.; FesΓÇÖko, V. *Russian Journal of Physical Chemistry A, Focus on Chemistry* **2012,** *86,* 170-174.

(33)   Rozenthal *Bulletin des Soci+®t+®s chimiques belges* **1936,** *45,* 621.

(34)   Bonhorst, C. W.; Althouse, P. M.; Triebold, H. O. *Industrial & Engineering Chemistry* **1948,** *40,* 2379-2384.

(35)   Schlenk *Justus Liebigs Annalen der Chemie* **1969,** *727,* 1.

(36)   Silbert, e. a. *Journal of the American Chemical Society* **1959,** *81,* 3244.

(37) National Institute of Standards and Technology. NIST Chemistry WebBook. NIST Standard Reference Database Number 69. 1-2-2010. U.S. Secretary of Commerce on behalf of the United States of America. 21-2-2010.
Ref Type: Online Source

(38) Domanska *J. Chem. Eng. Data* **1999,** *44,* 974.

(39) American Petroleum Instititute *Chemical Abstracts* **1946**.

(40) Schiessler, R. W. e. al. *Amer. Doc. Inst* **1945**.

(41) Prosen, E. W.; Rossini, F. D. *Journal of Research of the National Bureau of Standards* **1945,** *38,* 263-267.

(42) Constantinou, L.; Gani, R. *AIChE J.* **1994,** *40,* 1697-1710.

(43) Energy Institute (Institute of Petroleum). IP 12: Determination of specific energy. 2001. Energy Institute.
Ref Type: Generic

(44) Ban-Weiss, G. A.; Chen, J. Y.; Buchholz, B. A.; Dibble, R. W. *Fuel Processing Technology* **2007,** *88,* 659-667.

(45) Szybist, J. P.; Boehman, A. L.; Taylor, J. D.; McCormick, R. L. *Fuel Processing Technology* **2005,** *86,* 1109-1126.

(46) Mueller, C. J.; Boehman, A. L.; Martin, G. C. *SAE Technical Paper Series* **2009,** 2009-01-1792.

(47) Turns, S. *An introduction to combustion: Concepts and Applications;* McGraw Hill: 2000.

(48) Tree, D. R.; Svensson, K. I. *Progress in Energy and Combustion Science* **2007,** *33,* 272-309.

(49) Ladommatos, N.; Rubenstein, P.; Bennett, P. *Fuel* **1996,** *75,* 114-124.

(50) Benjumea, P.; Agudelo, J. R.; Agudelo, A. ü. F. *Energy Fuels* **2010,** *25,* 77-85.

(51) McCormick, R. L.; Graboski, M. S.; Alleman, T. L.; Herring, A. M.; Tyson, K. S. *Environmental Science & Technology* **2001,** *35,* 1742-1747.

(52) Fisher, B. C.; Marchese, A. J.; Volckens, J.; Lee, T.; Collet, J. L. *SAE Technical Paper Series* **2011**.

(53) Szybist, J. P.; Song, J.; Alam, M.; Boehman, A. L. *Fuel Processing Technology* **2007,** *88,* 679-691.

(54) Emran, S. K.; Newkome, G. R.; Weis, C. D.; Harmon, J. P. *J. Polym. Sci. B Polym. Phys.* **1999,** *37,* 2025-2038.

(55) Yasunaga, K.; Simmie, J. M.; Curran, H. J.; Koike, T.; Takahashi, O.; Kuraguchi, Y.; Hidaka, Y. *Combustion and Flame* **2011,** *158,* 1032-1036.