

Effect of the Molecular Structure of Individual Fatty Acid Alcohol Esters (Biodiesel) on the Formation of NO_x and Particulate Matter in the Diesel Combustion Process

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ABSTRACT

Biodiesel is a renewable fuel which can be used as a direct replacement for fossil Diesel fuel as a calorific source in Diesel Engines. It consists of fatty acid mono-alkyl esters, which are produced by the trans-esterification reaction of plant oils with monohydric alcohols. The Plant oils and alcohols can both be derived from biomass, giving this fuel the potential for a sustainable carbon dioxide neutral life-cycle, which is an important quality with regard to avoiding the net emission of anthropogenic greenhouse gases. Depending on its fatty ester composition, Biodiesel can have varying physical and chemical properties which influence its combustion behaviour in a Diesel engine. It has been observed by many researchers that Biodiesel can sometimes lead to an increase in emissions of oxides of nitrogen (NO_x) compared to fossil Diesel fuel, while emitting a lower amount of particulate mass. The work described in this paper examines the influence of the detailed molecular structure of fatty acid ester molecules on the formation of NO_x and particulate matter. Several individual fatty acid alcohol esters were synthesised and tested as fuel in a single-cylinder direct injection Diesel engine under carefully controlled operating conditions. Cylinder pressure and exhaust gas emissions were measured and exhaust particulate number and size distribution were recorded using a differential mobility spectrometer. An ignition improving additive was used in certain experiments to eliminate the influence of ignition delay on the combustion characteristics of the various molecules. It was observed that the chain length and the degree of saturation of the fatty acids, as well as the type of alcohol used for the fuel synthesis, have distinct effects on the formation of NO_x and particulate matter during Diesel combustion.

INTRODUCTION

Biodiesel consists of ester molecules, which are produced by the trans-esterification reaction of plant oils or animal fats with monohydric alkyl alcohols. The molecular structure and synthesis process of Biodiesel molecules as fuel were formulated by Chavanne^[1], using the example of palmitic acid ethyl ester. Biodiesel consists of a mixture of a large variety of such molecules whose detailed composition depends on the types of fat or plant oils and the type of alcohol employed for the fuel synthesis. The molecular structure of the individual fuel molecules determines the ignition and heat release characteristics, as well as the progressive physical dispersion of the fuel within the combustion chamber and its mixing process with the surrounding air. These factors are known to govern the formation and decomposition of gaseous pollutants and particulate matter as well as the engine efficiency.

It has been known for some time that the combustion of Biodiesel tends to result in a higher amount of nitrogen oxides (NO_x) in comparison to fossil Diesel fuel^[2,3,4]. Several different explanations for this have been proposed in the literature, but it still not entirely clear why this increase is observed. The currently published literature suggests five major hypotheses:

1. Advance in injection timing due to the higher bulk modulus of Biodiesel.
2. High cetane number of Biodiesel advances the point of ignition and causes a history of higher cylinder temperatures within the cylinder.
3. Formation of 'prompt' (Fenimore) NO_x from high hydrocarbon radical concentration caused by double bonds in Biodiesel molecules.
4. Increase in actual flame temperature due to lower soot radiative heat transfer of oxygenated molecules.

5. Elevated adiabatic flame temperature of Biodiesel molecules, especially from unsaturated (double bonded) molecules.

The first theory states that a significant advance in injection timing occurs due to the higher bulk modulus of Biodiesel. This applies to engines with mechanically operated injection system in which the fuel is used as a medium of timing the injection by transmitting a pressure wave from the plunger of the pump to the injector. This theory is supported by the works of Ziejewski et al. (1985)^[5], Gouw and Vlughter (1964)^[6], Rolling and Vogt (1960)^[7], Tat et al. (2000)^[8], Monyem et al. (2001)^[9] and Szybist and Boehman (2003)^[10]. It was shown that the advance in injection timing positively contributes to higher NO_x emissions in engines operating with such mechanical injection systems. Studies carried out in common rail fuel systems showed that this phenomenon does not occur in modern electronically controlled common rail injection systems as was observed by Choi et al. (1997)^[11], Zhang and Boehman (2007)^[12] and Cheng et al. (2006)^[13].

The second theory suggests that the higher cetane number of Biodiesel advances the point of ignition and causes a history of higher cylinder temperatures within the cylinder. It has been shown by many researchers (Ladommatos et al. (1996a)^[14], McCormick et al. (2002)^[15] and Szybist et al. (2003)^[10]) that NO_x emissions tend to decrease with higher ignition quality of Diesel fuel and Biodiesel. Thus this theory does not appear to be sustainable for most engine applications.

The third theory suggests that the formation of 'prompt' NO_x (which shall be referred to as 'Fenimore' NO_x in this article) is higher for Biodiesel fuel than for Diesel fuel. This is suggested to be due to a higher concentration of fuel derived hydrocarbon radicals, which are relevant to the formation of Fenimore NO_x. Ban-Weiss et al. (2007)^[16] showed in a modeling study that the relative effect of Fenimore NO_x is smaller than the thermally motivated Zeldovich NO_x. Yet, the modeling showed that Fenimore NO_x is responsible for approximately 13% of total NO_x formed from the combustion of methyl butanoate, which is a very short-chained fatty acid ester molecule. This amount is of the order of the observed increase in NO_x for Biodiesel fuels versus Diesel fuel, so this theory could potentially account for most of the observed increase in NO_x.

The fourth theory suggests that the actual flame temperature of Biodiesel is higher than those of fossil Diesel fuel due to lower soot radiative heat transfer from Biodiesel flames. Optical experiments carried out by Cheng et al. (2006)^[13] could be supportive of this theory and it also agrees with the observations made by several researchers (Pischinger et al. (1982)^[2], Mittelbach et al. (1985)^[4], Schumacher et al. (1996)^[17], Graboski and McCormick (1998)^[18]), that Biodiesel has a lower propensity to form particulate matter, but raises NO_x emissions. However, there is evidence in the literature and in the results presented in this paper which tends to contradict this theory: For example, results will be shown in this paper for unsaturated fatty acid esters which exhibit higher NO_x emissions as well as higher

particulate mass emissions than more saturated molecules. This would tend to disagree with the theory that fuels with lower soot emissions produce higher NO_x emissions only due to lower soot radiative heat transfer. This argument is somewhat supported by fundamental studies carried out on diffusion flames, which show that unsaturated alkenes have a higher propensity to form soot during combustion than saturated alkanes (Ladommatos et al., 1996b)^[19]. These two observations together tend to contradict the theory that flames from hydrocarbons which produce lower soot also always produce higher amounts of NO_x, because unsaturated molecules are known to produce more soot, but yet they also produce higher amounts of NO_x.

A fifth hypothesis was advanced by Ban-Weiss et al. (2007)^[16]. It states that unsaturated Biodiesel molecules, cause an increase in adiabatic flame temperature compared to fossil Diesel fuel. The authors carried out a comparison in the adiabatic flame temperature between two molecules methyl butanoate and methyl trans-2-butenoate, which are representative of Biodiesel molecules. The peak flame temperature of the double-bonded methyl trans-2-butenoate was found to be 14 K higher than that of the saturated methyl butanoate. This increase in adiabatic flame temperature resulted in an increase of 21% of NO_x emissions according to the numerical model.

The work described in the present study is aimed at experimentally investigating the influence of the molecular structure of fatty acid alcohol esters on the combustion process in a Diesel engine, with particular attention given to their propensity of forming NO_x and particulate matter.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experiments were carried out in a single-cylinder direct-injection research Diesel engine based on the Ricardo Hydra design. The engine was constructed using the cylinder head, piston and fuel injector of a production 2.0L Ford Puma automotive Diesel engine to provide a combustion chamber geometry representative of a production Diesel engine. The compression ratio was 15:1. The intake air was naturally aspirated into the cylinder. The crank angle was monitored using an optical shaft encoder driven directly by the engine crankshaft with 1800 pulses per revolution. The cylinder pressure was sampled at intervals of 0.2 degrees crank angle using a Kistler 6056AU38 piezoelectric pressure transducer and a Kistler Type 5011 charge amplifier. The concentration of gaseous exhaust emissions was measured using a Signal gas analysing system (chemiluminescence for NO_x, NDIR for CO and CO₂, and FID for unburned hydrocarbons), while particulate size distribution and number were measured using a Cambustion DMS500 differential mobility particulate spectrometer. The engine crankshaft was coupled to a DC dynamometer whose control system allowed motoring and braking of the engine and constant speed operation at all engine loads.

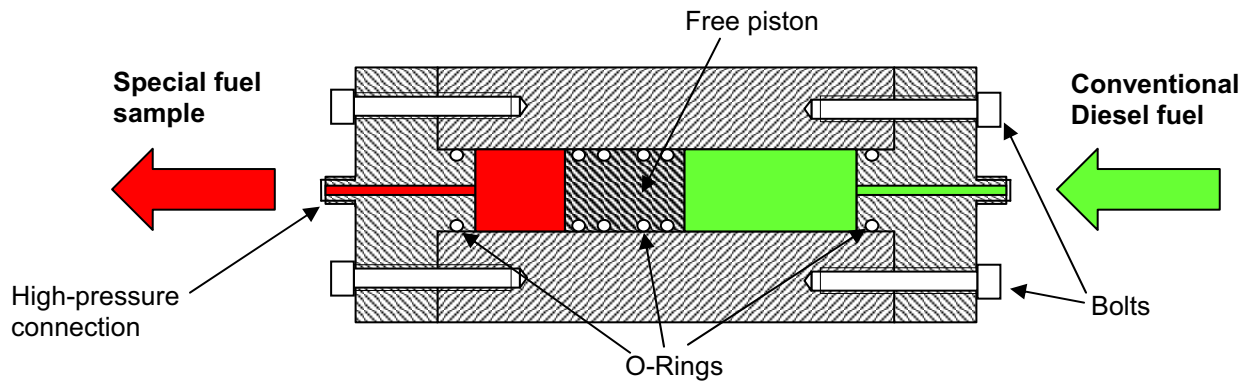


Figure 1 – Schematic of the free-piston cylinder used to transmit the common rail pressure onto the test fuel samples

ULTRA LOW VOLUME FUEL INJECTION SYSTEM - The samples of the individual fatty acid alcohol esters were purposely synthesised for these experiments and were only available in small quantities. Such small quantities did not suffice to fill a modern Diesel fuel injection system consisting of fuel pump, common rail, connection pipes and filter. Furthermore, several of the individual fatty acid alcohol esters were solid at room temperature, and required accurate temperature control during injection to insure that they could be injected in liquid form and at a specified temperature. These restrictions prevented the use of a commercial Diesel fuel pump to pressurise the fuel samples directly, even if sufficient fuel had been available.

achieving injection pressures of up to 160 MPa and fuel temperature control within 2 K. The concept of this system was to use a common-rail Diesel fuel system running on conventional Diesel fuel to generate the injection pressure, without the conventional Diesel fuel actually taking part in the combustion. Thus, the standard common rail Diesel fuel system of the engine was used to control the pressure of a separate low-volume fuel delivery system containing a small fuel sample. A stainless steel hydraulic cylinder with a centrally located free-piston was developed to satisfy these requirements (see Figure 1).

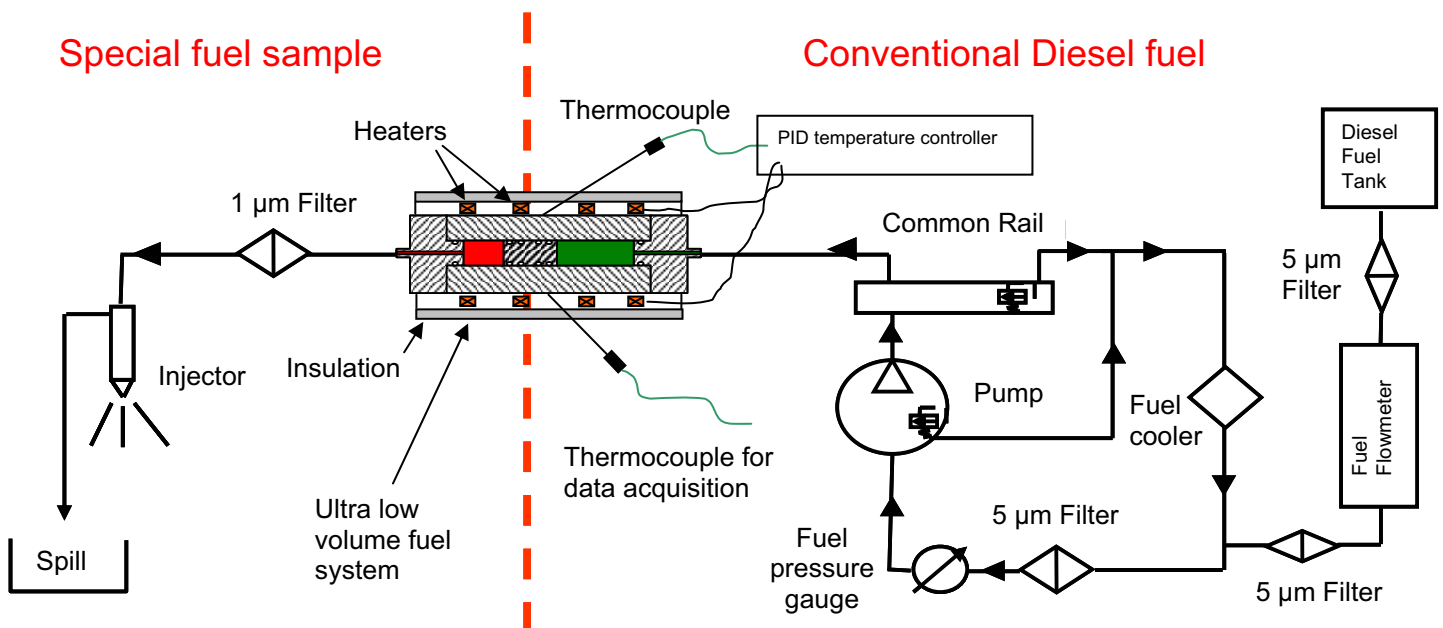


Figure 2 – Schematic of the complete fuel injection system

A special fuel delivery system was developed which allowed small quantities of fuel to be injected with accurate control of fuel temperature and injection pressure through the engine's commercial solenoid injector. The system was capable of running engine tests with fuel-samples of less than 100 ml per test,

The cylinder was designed to withstand the maximum common rail pressure (160 MPa), and carried high pressure connections for fuel pipes at both ends. It was divided into two chambers by a centrally located free piston which was able to move along the axis of the cylinder. The piston sealed the two opposing chambers against each other via four o-rings around its circumference. One of the chambers was filled with the special fuel small sample under investigation, while the

other chamber was fed with standard Diesel fuel which was supplied and pressurised through the standard engine common rail fuel system. Because the piston was free to move along the cylinder axis, it transmitted the pressure from the fuel in the common rail directly onto the fuel sample without allowing any mixing of the two liquids to take place. Due to the free-piston having very little friction and only travelling at low velocities, the pressure in both chambers reached a state of near equilibrium, so that virtually no pressure differential exists across the piston. The operation of the remaining fuel system was similar to that of a standard common rail system used in production Diesel engines. The main components were the high-pressure Diesel fuel pump, the common rail, a fuel cooler, a fuel tank and a fuel flow-meter (see Figure 2). The pump fed the common-rail with conventional Diesel fuel at high pressure, which in turn supplied the right-hand chamber of the ultra low volume fuel injection system with conventional Diesel fuel at the same pressure. The conventional automotive Diesel fuel was used as the hydraulic medium to pressurize the small sample of test fuel. Any Diesel fuel returned from the common rail and the pump, was cooled in the fuel cooler and directly returned to the inlet of the high-pressure pump. The consumption of the small quantity of sample fuel by the engine caused the free piston in the stainless steel cylinder to move to the left (see Figure 1 and Figure 2), thus increasing the capacity of the normal Diesel fuel within this cylinder, on the right side of the free piston. This caused a flow of fresh fuel supplied into this circuit from the normal Diesel fuel tank which was measured using a positive-displacement piston flow-meter. The spill-flow of the sample fuel from the injector was measured so that it could be subtracted from the total fuel consumption to yield the amount of fuel injected into the combustion chamber.

EXPERIMENTAL PROCEDURE – Before every experiment, the free-piston fuel system was dismantled and cleaned. During re-assembly, the free-piston was positioned at the right-most side of the cylinder (see Figure 1), so that the volume of the chamber on that side of the cylinder was reduced to its clearance volume, and the other side (fuel sample side) was at its maximum volume. The right side (see Figure 1) was then connected to the common rail of the engine via a high-pressure pipe so that it could be supplied with normal high-pressure Diesel fuel from the common rail. The chamber on the left side of the cylinder, which now had the larger volume, was filled-up with the single-molecule fuel sample. This chamber was then connected to the solenoid injector on the engine via a high-pressure Diesel fuel pipe which contained a 1µm filter element to protect the injector. The fuel system was held at a constant temperature of 353 K ± 2K via an electronically proportional-integral-derivative (PID) controlled heating system installed on the fuel injection system. Once all pressure connections were secured, the engine was motored to the required speed using the engine dynamometer control system. The common-rail pressure (and hence the small fuel test sample pressure) and the injection timing for the small fuel test sample were adjusted electronically via the engine control system. All experiments were carried out at 1200 rpm, and at a constant indicated work output per cycle corresponding to 0.4 MPa IMEP. The injection pressure used in all experiments was of 45 MPa.

TYPES OF MOLECULES INVESTIGATED – The experiments were conducted on eight fatty acid alkyl esters, to investigate the effect of three different properties of the molecular structure. The effect of chain length, number of double bonds and the type of alcohol used in the synthesis were studied. Physical and chemical properties of the fuels are given in Table 1.

		Diesel fuel	C12:0 Methyl laurate	C14:0 Methyl myristate	C16:0 Methyl palmitate	C18:0 Methyl stearate	C18:1 Methyl oleate	C18:2 Methyl linoleate	C22:0 Methyl behenate	C18:1 Ethyl oleate	2-EHN
Upper heating value	<i>kJ/kg</i>	45820	37913	38852	39119	40210	40032	39613	41631	-	-
Lower heating value	<i>kJ/kg</i>	42980	35306	36202	36443	37501	37436	37148	38872	-	27364 ^[25]
Carbon (calculated)	%	-	72.84	74.32	75.50	76.45	76.97	77.49	77.9	77.36	54.84
Hydrogen (calculated)	%	-	12.23	12.48	12.67	12.83	12.24	11.64	13.08	12.34	9.78
Oxygen (calculated)	%	-	14.93	13.20	11.83	10.72	10.79	10.87	9.02	10.3	27.39
Nitrogen (calculated)	%	-	0	0	0	0	0	0	0	0	7.99
Carbon (measured)	%	86.68	73.02	74.35	-	-	76.99	77.43	-	-	-
Hydrogen (measured)	%	13.32	12.23	12.44	12.57	12.73	12.20	11.58	-	-	-
Oxygen (measured)	%	0.07	14.76	13.21	-	-	10.80	10.99	-	-	-
Density @ 15°C	<i>g/ml</i>	0.8342	0.873	0.870	-	-	0.896	0.891	-	-	0.963
Viscosity @ 40 °C (*20% vol. sample in Diesel fuel)	<i>mm²/s</i>	2.564	2.425	3.273	2.778*	2.986*	4.518	3.745	-	-	-
Cetane No.	-	49.8	62 ^[20]	71 ^[20]	81 ^[20]	89 ^[20]	62 ^[20]	42 ^[20]	-	65 ^[20]	-
Normal B.Pt.	°C	-	262 ^[26]	323 ^[26]	338 ^[26]	352 ^[26]	349 ^[26]	366 ^[26]	394 ^[26]	-	-
Melting Point	°C	-	4.5-5	18	32-35	37-41	-20	-35	-	-32	-

Table 1 – Physical and chemical fuel properties

EXPERIMENTAL CONDITIONS

Constant injection timing:

	I.M.E.P.	Engine speed	Injection timing [deg CA BTDC]	Ignition timing [deg CA BTDC]	Injection pressure
	[bar]	[rpm]			[bar]
EN 590 Diesel	4.00	1200	7.1	TDC	450
C12:0 M	4.00	1200	7.1	0.4	450
C14:0 M	4.00	1200	7.1	0.8	450
C16:0 M	4.00	1200	7.1	1.6	450
C18:0 M	4.00	1200	7.1	1.8	450
C22:0 M	4.00	1200	7.1	1.0	450
C18:1 M	4.00	1200	7.1	-0.2	450
C18:2 M	4.00	1200	7.1	-2.0	450
C18:1 E	4.00	1200	7.1	-0.3	450
EN 590 Diesel	4.00	1200	7.1	TDC	450

Constant ignition timing:

	I.M.E.P.	Engine speed	Injection timing [deg CA BTDC]	Ignition timing [deg CA BTDC]	Injection pressure
	[bar]	[rpm]			[bar]
EN 590 Diesel	4.00	1200	7.1	TDC	450
C12:0 M	4.00	1200	7.4	TDC	450
C14:0 M	4.00	1200	7.2	TDC	450
C16:0 M	4.00	1200	6.8	TDC	450
C18:0 M	4.00	1200	6.3	TDC	450
C22:0 M	4.00	1200	6.7	TDC	450
C18:1 M	4.00	1200	7.5	TDC	450
C18:2 M	4.00	1200	9.0	TDC	450
C18:1 E	4.00	1200	7.6	TDC	450
EN 590 Diesel	4.00	1200	7.1	TDC	450

Constant ignition delay:

	I.M.E.P.	Engine speed	Injection timing [deg CA BTDC]	Ignition timing [deg CA BTDC]	Injection pressure	2-EHN treatment rate
	[bar]	[rpm]			[bar]	[vol. %]
EN 590 Diesel	4.00	1200	6.2	TDC	450	1.83
C12:0 M	4.00	1200	6.2	TDC	450	1.00
C14:0 M	4.00	1200	6.2	TDC	450	0.45
C16:0 M	4.00	1200	6.2	TDC	450	0.10
C18:0 M	4.00	1200	6.2	TDC	450	0.00
C18:1 M	4.00	1200	6.2	TDC	450	1.60
C18:2 M	4.00	1200	6.2	TDC	450	3.42
C18:1 E	4.00	1200	6.2	TDC	450	1.40
EN 590 Diesel	4.00	1200	6.2	TDC	450	1.83

Table 2 – Experimental engine running conditions

EXPERIMENTAL RESULTS

The following section describes the experimental results recorded in this study. These are divided into three main sections, according to the type of structural effect of the molecules studied. These are:

1. Fatty acid chain length
2. Degree of saturation
3. Alcohol chain length

The results are further divided into *three experiments* for each structural effect studied. The first experiment examines the behavior at **constant injection timing** for all fuel samples. The time of injection was chosen so that ignition would occur at TDC for standard fossil Diesel fuel. In the second experiment the injection timing is optimised in each experiment to yield **constant ignition timing** at TDC for all fuels. In a third set of experiments, the fuel samples were additised with the ignition improving additive 2-ethylhexyl nitrate (2-EHN) in different amounts, in order to obtain a constant time of injection as well as a constant time of ignition for all fuel samples. This allowed having a **constant ignition delay** for all fuel molecules. Details of the experimental conditions are given in Table 2.

FATTY ACID CHAIN LENGTH - The first set of experiments was conducted to study the effect of chain length of the fatty acid ester molecules upon the Diesel combustion process. The results were compared with the combustion of fossil Diesel fuel-oil (EN 590 standard) used to bracket the experiments. The tests with the fossil Diesel fuel were carried out before the Biodiesel molecules were tested, and they were then repeated after the tests on the Biodiesel molecules. This was done to provide a basis for comparison, and an indication of repeatability of the results. Clear differences in the ignition characteristics of the individual fatty acid alkyl ester fuel molecules were observed which correlated with fatty acid chain length of the molecules. Efforts were made to distinguish between effects caused by the ignition characteristics of the molecules and high temperature kinetic effects, by optimising the start of ignition of the fuel by both physical and chemical means. As mentioned above, three independent experiments were carried out: In the first experiment, all fuel molecules were injected at the same point during the Diesel cycle (7.1 deg CA BTDC). In the second experiment, the time of injection was optimised to yield a constant time of ignition at top dead centre of the Diesel cycle. In a third experiment, the fuel samples were additised with a small amount of an ignition improving molecule (2-ethylhexyl nitrate) which allowed achieving constant time of injection and ignition in the same experiment. This provided a constant time of injection as well as a constant ignition delay for all fuel samples and allowed focusing on effects other than that of ignition delay such as the influence of the chain length upon the high-temperature chemical kinetics.

Effect of fatty acid chain length studied in constant injection timing experiments - In the first experiment, five saturated fatty acid methyl esters were all injected at a constant point during the Diesel cycle. The fuel quantity was adjusted so that their respective combustion resulted in a constant amount of indicated work per engine cycle (0.4 MPa IMEP). The fuel was injected at 7.1 degrees (deg) crank angle (CA) before top-dead-centre (BTDC). This is the injection timing which was optimised so that standard fossil Diesel fuel would start combustion at top-dead-centre (TDC). The combustion of the mentioned individual fatty acid methyl esters was compared in the same experiment with that of fossil Diesel fuel. Figure 3 shows the cylinder pressure, heat release rate, and mass fraction burnt of the experiment.

A clear trend can be observed for all fatty acid alkyl esters containing 12 to 18 carbon atoms in their fatty acid shown in Figure 3. A longer fatty acid chain length results in better ignition quality of the fuel molecule, and earlier ignition of the fuel. Earlier ignition implies that the ignition delay between injection of the fuel and ignition of the fuel is shortened. This is reflected in a smoother heat release pattern of the fuel, and a shift from premixed combustion towards diffusion controlled combustion. This can be observed in the central graph on Figure 3, where it is visible that for long-chained molecules not one heat release rate peak is visible, but two distinct peaks. The first peak represents the mainly premixed combustion phase, while the second peak indicates mainly diffusion controlled combustion. A larger degree of pre-mixed combustion is usually associated with higher NO_x emissions and lower particulate mass emissions. This is due to the following reasons: Consider the lower part of Figure 3 which shows the mass fraction burnt of the injected fuel, and gives a good indication of combustion duration. The longer chained molecules burn for a longer period of time with a lower peak heat release rate and induce lower peak global pressures in the combustion chamber as can be seen in the graph at the top of Figure 3. Lower global cylinder pressures usually imply lower combustion temperatures and result in a reduced formation of NO_x, because NO_x is usually formed at high temperatures (mainly above 2000 K)^[23]. Further to this, the patterns of stoichiometry of the combustion process are changed due to a shift from more pre-mixed combustion towards diffusion combustions with shorter ignition delay and shorter flame lift-off lengths.

Figure 4 shows the gaseous pollutant emissions recorded in the exhaust gas of the engine. It is visible that the NO_x concentration for all fatty acid alkyl esters is below that of standard Diesel fuel for these experiments. A clear trend in the detailed effect of the fatty acid chain length of the ester is visible on the NO_x emissions, when using constant injection timing. An increase in the chain length was observed to result in lower NO_x emissions when the fuels are injected at a constant timing during the cycle. This can to a large extent be explained by the heat release characteristics of the various molecules as previously described: The longer chained fatty acid alkyl

esters have a tendency to ignite more quickly after they are injected into the combustion chamber. This has been shown to result in a heat release pattern which is moderated by the fuel and air mixing process, as can be seen in Figure 3. This more moderated heat release rate of long chained molecules results in lower peak flame temperatures, which have a reduced ability to produce NO_x .

Optical studies on the combustion of Diesel fuel sprays have shown that the ignition quality not only affects the ignition delay of the fuel, but also the flame lift-off length of the fuel spray^[13]. The flame lift-off length influences the local combustion stoichiometry by altering the pattern of fuel air mixing in the fuel spray. A shorter flame lift-off length allows less fuel and air mixing to take place prior to combustion, thereby limiting the combustion rate by diffusion mixing. The reduced air-entrainment of the fuel-spray aids the formation of particulate matter due to fuel pyrolysis within the rich core regions of the spray. A shift in the combustion mechanism towards a diffusion controlled combustion mode has been shown to increase the probability of soot formation within the flame^[14].

It was observed, that all fatty acid methyl esters emitted significantly less particulate mass than the fossil Diesel reference fuel. The higher particulate mass for Diesel fuel originates from the larger number of accumulation mode particles (50-200 nm) produced. The lower emission of particulate mass from Biodiesel is likely to be an effect of its higher oxygen content, which aids the oxidation of soot particles and its precursors. No conclusive trend was observed for the level of total particulate mass emitted amongst the saturated fatty acid methyl esters with fatty acid chain lengths between 12 to 18 carbon atoms. The behenic acid methyl ester which contains 22 carbon atoms in its fatty acid chain did however show a distinctively higher emission of particulate mass, than the other molecules with lower fatty acid chain lengths. This is likely to have been due to spray formation and fuel-air mixing being affected by the very high viscosity and low volatility of this fuel. An interesting trend was observed for the number of nucleation mode particles of the size order of 5-50 nm (Figure 6). A progressively higher number of nucleation mode particles was recorded for fatty acid esters with longer fatty acid chain lengths. The average size of the particles in this mode, as well as their number seemed to be progressively increasing for molecules with a fatty acid chain from 12 to 22 carbon atoms. It is possible that the particles recorded in this mode actually consist of unburned fuel droplets which condensed in the exhaust gas due to the increasingly high boiling point of these fuel molecules. The experimental error of the exhaust gas analyses was estimated to be 2.5% for NO_x , 8% for UHC, 5% for CO, 1.5% for CO_2 , 0.5% for O_2 and 1% for particulate mass emissions. Engine load was estimated to be accurate to within 0.5%.

Effect of chain length studied in constant ignition timing experiments - In the previously described experiment, the start of injection of all fuels was induced at a constant time during the engine cycle. This ensured that

the combustion chamber properties were held constant at the time of injection. It was observed that the varying ignition characteristics of the individual fuel molecules significantly influenced the global pressure and temperature histories within the combustion chamber and lead to significant differences in pollutant formation. In order to harmonise the time of ignition for all fuels and to allow the start of ignition to take place in the same cylinder volume, the injection timing was adjusted individually for all fuels, so that their ignition would always occur at top-dead-centre. Figure 7 shows the cylinder pressure, heat release and mass fraction burnt histories during the combustion.

The experiments showed a similar heat release pattern as for the constant injection timing experiments (Figure 3 and Figure 7). The peak heat release rates of the longer chained molecules are increasingly moderated by the shorter ignition delay, and a shift from premixed combustion mode to diffusion combustion mode is visible in the heat release shape. The fuel samples with slower combustion rates exhibit a slightly longer burn duration, and show slightly higher cylinder pressures towards the later parts of the expansion stroke whereby the same useful engine work as for the other fuel samples is achieved. The peak cylinder pressures and temperatures for the longer chained molecules with moderated heat release rates are significantly lower than for the shorter molecules with a longer ignition delay. The exhaust gas analysis of the individual experiments can be seen in Figure 8.

The exhaust gas analysis shows that all saturated fatty acid methyl esters produced lower NO_x emissions than standard Diesel fuel. A clear trend can be seen in specific NO_x emissions between the individual fatty acid alcohol molecules. The longer the length of the fatty acid chain, the lower is the amount of NO_x produced even when the injection timing was optimised such that the start of ignition occurs at top dead centre for all fuels.

The particulate matter analysis (Figure 9 and Figure 10) shows that although the trend is very similar to the experiments with constant injection timing, the general particulate emission level for the fatty acid methyl esters is higher than for the constant injection timing. It was observed, that all fatty acid methyl esters produced significantly less particulate matter than the fossil Diesel reference fuel. Within the accuracy of the experiments no substantial effect of the chain length upon the particulate mass emissions could be observed for the saturated fatty acid methyl esters of twelve to 18 carbon atoms. The fatty acid methyl ester of 22 carbon atoms however did produce significantly higher particulate mass emissions than the other molecules. This is likely to have been due to the high viscosity and low volatility of the fuel.

Effect of fatty acid chain length studied in constant ignition delay experiments with additive addition - The

last two experiments were performed first at constant injection timing and then at constant ignition timing for all fuel molecules. In both experiments, the ignition delay was found to be significantly different for each fuel sample. This was observed to be a result of the

molecular structure of each type of fuel molecule and can be explained by each molecule's characteristic ability to decompose and initiate ignition. The ignition delay significantly affected the combustion behavior in terms of heat release rates and gaseous pollutant emission. The question arises how the individual molecules would behave during the Diesel combustion if their ignition behavior, and thus their physical fuel and air mixing was similar. This effect can be studied by adding an ignition promoting additive to the fuel in small quantities to harmonise the ignition delay of all fuel samples. This means that both the time of injection and the time of ignition are similar for all fuel molecules. Ideally, such a molecule would be used which breaks down at low temperature to promote ignition, but does not influence the high temperature chemistry of the combustion. It has been shown that the molecule 2-ethylhexyl nitrate (2-EHN) is effective at achieving such an effect when used in small concentrations^[22]. The fuel samples were additised by 2-EHN in varying amounts to yield a closely matched ignition delay for all fuel samples. This meant that both the injection timing and ignition timing could be held constant at the cost of adding an ignition promoting additive.

The cylinder pressure, heat release rates and mass fraction burnt can be seen in Figure 11. It can be observed that the pressure history is very similar for all fuels but on close observation it is visible that the combustion of fossil Diesel fuel results in higher cylinder pressures during the early stages of combustion (during the first 5 deg CA after TDC). This can be explained by looking at the heat release characteristics of the fuels which are displayed in the centre graph of Figure 11. It is clearly visible that the fossil Diesel fuel produces the highest heat release rate during the pre-mixed combustion phase, and less heat release in the later stages of combustion usually referred to as the diffusion controlled combustion phase. This is likely to be an effect of the higher calorific value, the lower fuel viscosity and the higher front end volatility of Diesel fuel compared to the fatty acid methyl ester molecules. The injection duration used for the Diesel fuel was shorter than that used for the Biodiesel molecules at the same engine load (0.4 MPa IMEP). This is because the higher calorific value and lower viscosity of the Diesel fuel are likely to result in a higher rate of injection of fuel energy into the combustion chamber. The higher front-end volatility of the diesel fuel is likely to contribute to a further increase of the mixing rate of the fuel with the air, so that for a constant ignition delay, this resulted in an increased amount of the fuel being ready for combustion in premixed combustion mode. Better atomization of the Diesel fuel in comparison to the Biodiesel fuel samples is likely to add to this effect by improving the fuel-air mixing.

The exhaust gas analysis is represented in Figure 12. It can be seen that now that the ignition delay is held constant, the differences in the emissions characteristics have been reduced between the fuels. The NO_x emissions still show a clear trend amongst the fatty acid alcohol esters but in the opposite direction than observed before, due to the removal of the effect of the

ignition delay. The longer chained fatty acid alcohol esters produced higher NO_x emissions than the shorter chained molecules.

This is a very interesting observation, because it suggests that the lower NO_x emissions from the Biodiesel molecules with longer fatty acid chains, is caused by differences in their ignition characteristics. It shows that the shorter ignition delay, which the longer-chained molecules experience due to their higher ignition quality in the constant injection timing and constant ignition timing experiments, plays a dominant role in the formation of NO_x. The third experiment in which the ignition delay was adjusted, removes this effect and highlights a secondary effect which had previously been masked by the prevailing role of the global heat-release patterns and stoichiometry, that are mainly controlled by the ignition delay.

It is also remarkable that the shorter-chained molecules which were treated with higher concentrations of 2-EHN (which introduces fuel-bound nitrogen to the fuel samples) actually produced lower amounts of NO_x than those fuel samples containing lesser amounts of 2-EHN. This indicates that fuel-bound nitrogen plays a comparatively small role in NO_x formation when used in the present concentrations. This also supports the use of 2-EHN as a research tool for controlling the ignition quality of fuel samples even when studying the formation of NO_x.

The total particulate matter emissions recorded during these experiments is shown in Figure 13. It was observed that within the accuracy of the experiment no conclusive trends could be seen in terms of total particulate mass generation between the individual fuel molecules. It appears that for fatty acid chain lengths between twelve and 18 carbon atoms, the chain length has a very small effect on the generation of total particulate mass. The behenic acid methyl ester was excluded from this set of experiments because in this way, all fuel samples (including those used in the experiments on the degree of fatty acid saturation and alcohol chain length) could be additised to match the ignition delay of the stearic acid methyl ester.

A more interesting effect can be observed when considering the effect of the chain length of the fatty acid alcohol ester upon the particulate size distribution (Figure 14). This shows clearly why the total particulate mass generated by the fossil Diesel fuel is much greater than that produced by the fatty acid alcohol esters. The fossil Diesel fuel produces a significantly higher number of accumulation mode particulates of up to 220 nm in diameter, while the Biodiesel molecules do not generate any significant amounts of particulate matter above 120 nm in size. This difference in emission of relatively large particles causes the difference in total emitted particulate mass between fossil Diesel fuel and Biodiesel fuel molecules. Another important observation can be made from the particulate size distribution amongst the Biodiesel molecules in Figure 14: With increasing chain length of the fatty acids, it was observed that the number of small particulates recorded (in the order of 5-30nm) increased progressively while the number of large particulates remained relatively unaffected.