The compression ignition and exhaust gas emissions of fuel molecules which can be produced from lignocellulosic biomass: levulinates, valeric esters and ketones

Elina Koivisto*, Nicos Ladommatos‡a, Martin Gold‡b

a Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom
b BP plc, Fuels and Lubricants Research, Technology Centre, Whitchurch Hill, Pangbourne, Reading, RG8 7QR, United Kingdom

E-mail addresses: elina.koivisto.11@ucl.ac.uk, elina.koivisto3@gmail.com

Tel: +44 (0)20 7679 3907
Fax: +44(0)20 7679 0180

KEYWORDS
Fuel molecular structure; lignocellulosic fuel molecule; diesel ignition delay; fuel effect on NOx; particulate emissions

ABSTRACT
This paper presents the results of combustion experiments conducted in a single cylinder compression ignition engine with several fuel molecules which can be produced from lignocellulosic biomass through a variety of processing routes. The lignocellulosic fuel
molecules tested were ethyl levulinate, butyl levulinate, ethyl valerate, butyl valerate, pentyl valerate, 5-nonanone, 3-heptanone, dipentyl ether and three alkanes. To ensure reliable compression ignition of all of the molecules, all of the molecules were tested after adding 30 wt-% of heptane to them. Levulinates were observed to have longer ignition delays than valeric esters, which in turn had longer ignition delays compared to ketones. All of the tested oxygenated molecules ignited later than the corresponding alkanes, excluding dipentyl ether. The differences in ignition delays where mainly attributed to the higher electronegativity of oxygen atoms compared to that of carbon and hydrogen atoms. The tested molecules, excluding 3-heptanone, had similar engine efficiency than to that of diesel fuel. However, the oxygenated fuel molecules resulted in higher NOx emissions and higher number of small particulates in exhaust gas emissions compared to alkanes and diesel fuel.

INTRODUCTION

Fuels made from lignocellulosic biomass are potential second generation biofuels. Lignocellulose includes the most abundant polymers on Earth and it is not likely to be a human food source. Lignocellulosic biomass includes agricultural and forestry residues, herbaceous energy crops and it can be found in municipal solid waste. However, breaking the strong structure of lignocellulose and converting it to biofuel molecules involves rather complicated processes. The relative difficulty in developing commercially feasible technologies to do this is the main reason why lignocellulosic biofuels are not currently widely produced until recently.

For example, the world’s first wood-based renewable commercial fuel production started commercial operation in UPM Lappeenranta Biorefinery in Finland in January 2015.

Lignocellulosic biomass can be converted into biofuels through thermal, biological and catalytic routes. The catalytic approach can be used to produce furfurals from lignocellulose through acid
hydrolysis. The furfurals can, in turn, be converted into several chemicals, polymers, bioalcohols (e.g. ethanol), gasoline octane busters (e.g. 2-methylfuran and dimethylfuran) and levulinic acid.

Levulinic acid is a versatile intermediate chemical, which can be processed further to produce biofuel molecules. The research for economical ways to produce levulinic acid from lignocellulose in large scale is ongoing: several possible pathways were described in the review articles by Rackemann and Doherty\(^4\) and Deng et al.\(^5\). Biofuel molecules such as 2-methylfuran, \(\gamma\)-Valerolactone, valeric esters and levulinates can be produced from levulinic acid\(^1\). A general chemical route to produce these biofuel molecules from lignocellulosic material is shown in Fig.\(^6\). Because esters are known to be viable biofuels for diesel engines\(^7\)–\(^9\), this study focused on the combustion of levulinates as well as valeric esters.
Figure 1. Production of levulinates and valeric esters from C6 sugars of lignocellulosic materials (adapted from [6]).

The levulinates are produced through esterification of levulinic acid and they have been proposed as fossil gasoline and diesel fuel extenders. When considering the physical properties of levulinates, methyl levulinates are potential gasoline additives, whereas ethyl and higher levulinates can potentially be used as diesel blend components. The boiling points of ethyl and higher levulinates are similar to those of the heavy gasoline compounds (over 475 K) and correspond to the middle of the diesel fuel boiling range. The low cetane numbers of levulinates limit their blend proportion in diesel blends. According to Joshi et al., diesel
blends with ethyl levulinate up to 15 v% satisfy the ASTM D6751 and have improved cloud point, pour point and cold filter plugging point compared to diesel fuel. However, Chuck and Donnelly \textsuperscript{13} concluded that butyl levulinate is a poor alternative for aviation kerosene because it is not miscible at low temperatures. Although several ways to produce alkyl levulinates have been developed, for example as described in a review article by Demolis et al. \textsuperscript{14}, only a small number of kinetic studies and engine studies are available on the oxidation of alkyl levulinates. Christensen et al. \textsuperscript{10} tested ethyl levulinate and butyl levulinate as diesel blends in a 2008 model year Cummins ISB engine. With 10 v% ethyl levulinate and 20 v% butyl levulinate blends they observed no change in total hydrocarbon, CO, or particulate matter exhaust gas emissions. The engine-out smoke number was reduced by 41.3\% and 55\%, respective of the two blends, while NO\textsubscript{x} emissions were observed to increase by 0\% and 4.6\%, respectively. Janssen et al. \textsuperscript{15} conducted experiments of 60, 70 and 80 v% butyl levulinate/tetradecane blends in a single cylinder research engine. They observed that a reduction up to 95\% (depending on the load) in particulate emissions could be achieved with butyl levulinate addition to tetradecane, compared to fossil diesel fuel. However, an increase was observed in hydrocarbon, CO and noise emissions for butyl levulinate/tetradecane blends compared to fossil diesel fuel. Nevertheless, Christensen et al. \textsuperscript{10} concluded that commercial applications of levulinates would be challenging due to their poor solubility in diesel fuel at low temperatures and their low cetane number.

An alternative to esterification of the levulinic acid and use of the esters in diesel fuel blends is the hydrogenation of levulinic acid into valeric acid, which can then be esterified to produce valeric esters \textsuperscript{13–16}. Compared to levulinates, valeric esters are less polar and have lower boiling points (Appendix I) and are therefore more appropriate to act as biofuels in blends with gasoline and diesel fuels \textsuperscript{16}. According to Lange et al. \textsuperscript{16}, 20 v\% of ethyl valerate in gasoline meets the
research and motor octane numbers of European gasoline specification (EN 228), whereas butyl valerates and higher valeric esters could be suitable for diesel blends. Lange et al. \(^ {16} \) reported that blends of pentyl valerate and diesel have higher volatility, compared to fatty acid methyl esters (FAME), and that blending pentyl valerate with diesel improved cold flow properties more than blends of FAME, although FAME also has a lower cetane number. Very few studies have investigated the combustion kinetics and engine combustion of valerates and levulinates, and in the case of valerates such studies are particularly scarce. Research on the oxidation of ethyl or higher esters is generally scarce, mainly because methyl esters are the dominant compounds of current biodiesel fuels and, therefore, currently a main research focus. Combustion kinetic schemes for ethyl valerate and butyl valerate have been proposed by Dayma et al. \(^ {17} \), while Contino et al. \(^ {18} \) investigated the combustion of butyl and pentyl valerates in a single cylinder PSA DW10 engine. Contino et al. \(^ {18} \) concluded that, compared to diesel fuel, neither 20 v% of butyl valerate or 20 v% pentyl valerate added to diesel fuel resulted in significant changes in exhaust gas emissions or engine performance, despite an increase in ignition delay.

In the study reported here two levulinates, three valeric esters, two ketones, an ether and three alkanes were tested in a single cylinder diesel research engine with the aim of improving the understanding of their combustion characteristics, especially the ignition delay, and exhaust gas emissions of these potential lignocellulose-driven fuel molecules. Ketones, namely 3-heptanone and 5-nonanone, were tested because valeric acid, which can be esterified to produce valeric esters, can also be ketonized to form 5-nonanone and the 5-nonanone can subsequently be upgraded into several different hydrocarbons (such as straight chain alkanes and their isomers) using an acid catalyst \(^ {1} \). These hydrocarbons include straight chain alkanes (e.g. nonane), and for this reason three such alkanes were tested in this study. Finally, an ether was included in the set
of fuels tested so as to provide a different way of interpretation of oxygen in the molecular fuel structure than that in ketones and esters. It should be noted that in order to ensure reliable compression ignition of all the tested molecules, some of which have low cetane numbers, all the tests were conducted with 30 wt-% heptane added to each of the molecules investigated. The results of this study can be used to aid in selecting what stage lignocellulose should be chemically modified so as to produce a viable biofuel molecule with optimal combustion characteristics and exhaust gas emissions.

1. EXPERIMENTAL METHODS

1.1 ENGINE

The tests were conducted on a direct injection compression ignition research engine, which was naturally aspirated. The engine parameters are listed in Table 1. The single-cylinder research engine was constructed with parts from a donor Ford Duratorq commercial engine (engine head, piston, connecting rod, and injector), so major aspects of the combustion and fuel injector systems were identical to those of the commercial engine. The cylinder gas pressure was measured by means of a piezoelectric transducer (Kistler 6056AU38), located in an engine glow plug adapter, and a charge amplifier (Kistler 5011). A piezo resistive pressure transducer (Druck PTX 7517-3257), located in the engine intake manifold 160 mm upstream of the intake valve, was used to detect a reference absolute pressure once per engine cycle at bottom dead center. The absolute pressure was used to provide an absolute pressure reference every cycle for the piezoelectric transducer pressure record. The cylinder pressure from the piezoelectric transducer was digitized every 0.2 crank angle degrees (CAD) by a data acquisition system, which was controlled by a shaft encoder which provided digitization trigger every 0.2 CAD and a cycle reference signal at top dead center (TDC). The digitized pressure records for one hundred
consecutive engine cycles were then averaged and this ensemble average pressure record at 0.2 CAD intervals was used for thermodynamic heat release rate analysis.

Table 1. Specifications of the naturally aspirated research engine.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of active cylinders</td>
<td>1</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>18.2 : 1</td>
</tr>
<tr>
<td>Displacement (cc)</td>
<td>499.56</td>
</tr>
<tr>
<td>Bore (mm)</td>
<td>86</td>
</tr>
<tr>
<td>Stroke (mm)</td>
<td>86</td>
</tr>
<tr>
<td>Number of valves</td>
<td>4</td>
</tr>
<tr>
<td>Maximum cylinder pressure (MPa)</td>
<td>15</td>
</tr>
<tr>
<td>Piston bowl design</td>
<td>ω - bowl</td>
</tr>
<tr>
<td>Injector type</td>
<td>6-hole (DELPHI DF1 1.3)</td>
</tr>
<tr>
<td>Injector control</td>
<td>1 μs steps (EMTRONIX EC-GEN 500)</td>
</tr>
<tr>
<td>High pressure fuel system</td>
<td>160 MPa common rail (BOCH CRS2)</td>
</tr>
</tbody>
</table>

Because some of the tested fuel molecules had limited availability and high purchase costs, an ultralow volume fuel system was used, which allowed engine runs with small fuel samples sizes (minimum 120 ml)\(^{19,20}\). The Ultralow Fuel Volume System (UFVS) dispenses of the engine conventional common rail fuel injection system and, instead, it operates as a separate low volume fuel injection system, supplying the engine fuel injector directly. However, although it dispenses of the conventional common rail system as a fuel injection system, it still utilizes the common rail system but only as a high pressure, highly controllable, hydraulic system to pressurize the UFVS. A typical test, using for example 200ml of sample fuel, would commence with the engine coolant and oil fully warmed up and the engine being motored for a while at test speed until various temperatures around the engine, including coolant and oil stabilized. Injection from the UFVS would then commence and maintained for a period of a few minutes until the engine IMEP and exhaust emissions have stabilized, after which data was collected for at least 100 consecutive engine cycles, lasting a further few minutes. Reaching stable engine operation
with around 200ml of fuel sample and collecting the necessary data, while the engine maintained
a stable level of IMEP and exhaust emissions did not pose significant difficulties. Further
information on the operation and testing with the UFVS can be found in references [19,20].
Additionally, a flow rate measurement system was used to measure the flow rate of fuel injected
into the combustion chamber \( ^{21} \). This measurement allowed the calculation of the fraction of fuel
combusted in the premixed-combustion mode, and the calculation of the thermal engine
efficiency as the indicated thermal efficiency.

1.2 ANALYSIS OF EXHAUST GAS EMISSIONS

The engine exhaust gas was sampled 180 mm downstream of the exhaust valves and led through
a heated line to two gas analyzers. The total mass and number of particles per unit volume as
well as the particle size distribution of the exhaust gas sample was measured with a Cambustion
DMS 500 differential mobility spectrometer system. A particle density of 1.77 g/cm\(^3\) was
assumed \( ^{22} \). A frequently calibrated MEXA 9100HEGR emission analysis system measured the
concentrations of nitrogen oxides (NO\(_x\)) by chemiluminescence, carbon monoxide (CO) by non-
dispersive infrared (NDIR), carbon dioxide (CO\(_2\)) by NDIR, oxygen (O\(_2\)) by paramagnetic
detector, and unburned hydrocarbons by flame ionization in the exhaust gas sample.

1.3 EXPERIMENTAL CONDITIONS

The experiments were conducted at an engine speed of 1200 rpm, an engine load of 4 bar
indicated mean effective pressure (IMEP), injection pressure of 600 bars and intake air heated to
393 K. Injection timing was kept fixed at 7.5 crank angle degrees before TDC. A reference diesel
fuel test was conducted at the above test conditions at the beginning and at the end of each test
day to create a long-term facility log. The data from these tests allowed the detection of any
changes or day-to-day drifts in the equipment or the instrumentation. Based on this log with reference diesel fuel, the long term mean value of the NO\textsubscript{x} emission was 807.24 ppm, the standard deviation of the mean NO\textsubscript{x} was 44.7 ppm and standard error of the mean 5.53 ppm. The corresponding values for the mass of particulate matter in the engine exhaust gas were 0.0081 µg/cc, 0.0013 µg/cc and 0.00066 µg/cc; and for the numbers of particulates in the engine exhaust gas they were 8.85*10\textsuperscript{7} N/cc, 3.90*10\textsuperscript{7} N/cc and 1.95*10\textsuperscript{7} N/cc, respectively.

1.4 DATA ANALYSIS

The heat release rate (HRR) used in the data analysis was the net heat release rate, which was considered as the difference between: chemical energy released to the engine cylinder contents by combustion minus the heat transfer from the engine cylinder contents to the combustion chamber surfaces, as shown in Heywood\textsuperscript{23}. The engine in-cylinder contents were assumed to be at uniform pressure and temperature and were modelled as an ideal gas. The percentage of the fuel that burned during the premixing controlled phase, denoted as premixed phase, was calculated as the ratio of: the cumulative HRR that occurred between SOC and the end of the premixed phase divided by the measured chemical fuel energy injected during the engine cycle. The end of the premixed phase was defined as the highest maximum value of the second derivative of HRR. The adiabatic flame temperature at constant pressure was calculated from iteration of the absolute enthalpy of the reactants at the initial in-cylinder temperature and that of the products at the adiabatic flame temperature. The iteration was conducted as presented by Turns\textsuperscript{24}. In the case of heptane blends, the heptane in the mixture was taken into account when calculating the adiabatic flame temperatures of the blends. Engine efficiency was considered as the indicated engine thermal efficiency, which was calculated as a ratio of: the indicated work output of the engine divided by the fuel chemical energy supplied to the engine during one
engine cycle. The reproducibility of the efficiency measurements was evaluated as described in section 1.3, above. Based on the set of 26 repeated tests with the reference diesel fuel, the long term mean value of the engine thermal efficiency was 45.6 %, the standard deviation of the mean value of the efficiency was 0.33% (percentage points) and standard error of the mean value of the efficiency was 0.065% (percentage points). The maximum average in-cylinder temperature, also known as global gas temperature, was calculated from the instantaneous in-cylinder temperature, which was calculated for any given time using the ideal gas law. The number of air moles present in the engine cylinder was estimated from the measurement of the air flow rate supplied to the engine. The values of in-cylinder temperature for hundred consecutive engine cycles were averaged for the calculation of net heat release rate and of the maximum average in-cylinder temperature.

1.5 FUEL MOLECULES INVESTIGATED

A number of fuel molecules, potentially obtainable from lignocellulosic biomass, were investigated; these molecules where two levulinates, three alkanes, three valeric esters, two ketones and an ether. Molecular structures of these molecules are shown in Fig. 2 and their physical properties are listed in Appendix I 25-29. Fig. 2 shows the molecules grouped in the following manner, so as to allow easier comparison of the results of these molecules: molecules on each column have the same carbon chain length (C7, C9 or C10); molecules on each row are from the same structural group.
Initially, ethyl levulinate, butyl levulinate, ethyl valerate and butyl valerate were tested each one on its own, as pure compounds, and none of these fuel molecules were observed to ignite in the diesel engine. Therefore, in order to enable reliable ignition, heptane was added to all the tested molecules. Heptane was selected as the ignition improver due to its similar combustion qualities compared to fossil diesel fuel. The amount of heptane added was the same (m%) for all molecules to allow comparison between the combustion chemistries of the molecules. The quantity of heptane in the blends was decided after further tests were conducted with ethyl levulinate, because it had the shortest carbon chain length and the highest oxygen content of the tested molecules; therefore, it was the most difficult molecule to ignite. Mixtures with 20, 30 and
40 wt-% added heptane by mass were tried. It was found that 30 wt-% of heptane was the
smallest amount of heptane that could be added to ethyl levulinate for reliable ignition, without a
pronounced two-stage ignition. To allow the results from all the fuel molecules tested to be
readily compared, 30 wt-% of heptane was added to all of the investigated molecules. The effect
of heptane on the combustion chemistry of the fuel mixtures is assumed to be similar in each test
for the purposes of this study, because the same amount (m %) of heptane was added to each one
of the molecules. Heptane interacts with the combustion of the molecules by donating radicals to
the combustion mixture and, due to the same amount of heptane in the mixture, similar amounts
of radicals from heptane may be expected to be available for each molecule at any given
temperature.

The objectives of the experiments were to investigate the effects on ignition and pollutant
emissions of the following structural changes in fuel molecules:

1. Adding a carbonyl group to an alkane to form a ketone.
2. Adding an ether linkage to an alkane to form an ether
3. Combining a carbonyl group and an ether linkage into an ester group to form a valeric
   ester
4. Adding a carbonyl group to the valeric ester to form a levulinate

2. RESULTS AND DISCUSSION

2.1 EFFECT OF MOLECULAR STRUCTURE ON IGNITION DELAY

Longer ignition delays generally allow greater time for fuel to evaporate and mix with air, and
therefore result in a greater portion of the injected fuel being burned rapidly close to TDC in
premixed-combustion mode. Fig. 3a shows, as expected, a positive correlation between the amount of premixed phase and ignition delay for alkanes and levulinates. Interestingly, ketones had a negative correlation and valeric esters no correlation between premixed phase and ignition delay when the premixed phase quantity was calculated as a percentage of energy injected, where the energy injected was defined as the chemical energy of the fuel injected during an engine cycle (Fig. 3a). The data presented in Fig. 3 is listed for each molecule in Appendix II. It is suggested, that the unexpectedly small premixed phases of the ketone 3-heptanone and the ethyl valerate (Fig. 3a) were caused by their lower percentages of total fuel combusted, compared to those of the other molecules in the same structural group. The lower combustion percentages resulted from the more difficult ignition of these molecules; for example, in the case of 3-heptanone only 61% of all the fuel energy was released during combustion, compared to the corresponding value of 89% for 5-nonanone. In the case of ethyl valerate only 90% of all the injected fuel energy was released during combustion, compared to the 99% for both butyl and pentyl valerate. It should be noted, that although the correlation between the ignition delay and premixed percentage within the structural groups was not positive for all the compounds (as one would expect), Fig. 3a shows that taken together, the data points for all compounds tested show a quite clear trend for the percentage of premixed combustion to increase when ignition delay becomes longer.
Figure 3. Effect of ignition delay on (a) premixed phase, b) in-cylinder temperature, (c) peak HRR and (d) timing of peak HRR.
Longer ignition delay was generally observed to result in higher in-cylinder temperature (Fig. 3b), higher peak HRR (Fig. 3c) and later timing of the peak HRR (Fig. 3d), as was expected. An exception to these trends was the levulinates, which did not show a rising peak HRR with increasing ignition delay (Fig. 3c). The lower peak HRR of ethyl levulinate compared to that of butyl levulinate (Fig. 3c) may be explained by the peak HRR occurring later in the expansion stroke for ethyl levulinate, as shown in Fig. 4 (see also Appendix II), where the combustion volume is greater. Nevertheless, despite combustion in a larger volume, ethyl valerate can be seen from Fig. 3b to reach a higher average combustion temperature. This can be explained by the substantially larger amount of premixed combustion of ethyl valerate (Fig. 3a).

Figure 4. Heat release rates of the tested molecules.

2.1.1 KETONES COMPARED TO ALKANES
The effect of adding a carbonyl group to an alkane to form a ketone was investigated by comparing 3-heptanone to heptane and 5-nonanone to nonane. Fig. 5a shows that ketones had longer ignition delays compared to the corresponding alkanes. These results were supported by the findings of a previous study \(^{30}\), in which six ketones were observed to have longer ignition delays than the corresponding alkanes. The later ignition of ketones, compared to alkanes, was suggested to be mainly caused by the oxygen atom in the carbonyl group of ketones. The carbonyl group is thought to affect the ignition delay mainly through the changes in the two main steps of the chemical ignition mechanism: H-abstraction and isomerization. Several studies \(^{31-34}\) have shown that the higher electronegativity of an oxygen atom, compared to that of carbon and hydrogen atoms, affects the strength of carbon-hydrogen bonds near the oxygen atom: the strength of the carbon-hydrogen bonds on the carbons next to the carbonyl group is weakened, but the strength of the carbon-hydrogen bonds on the next three carbon atoms of the chain are increased. Oxygen atom in the carbonyl group makes the overall H-abstraction from the oxygenated molecule more difficult than H-abstraction from the corresponding alkane molecules, thus increasing the ignition delay. In the case of isomerization, the rapid compression machine studies of Allen et al. \(^{35}\) have showed that carbonyl group hinders the formation of a transition ring during isomerization, compared to an alkane, and thus increases the ignition delay further. Furthermore, according to the low temperature oxidation experiments of Anderson and Hoare \(^{33}\) and Hoare and Li \(^{31}\), ketonyl peroxy radicals lead mainly to propagation reactions, instead of branching reactions through isomerization. This will contribute to the slower formation of a radical pool large enough to initiate and sustain ignition in the case of ketones compared to alkanes.
**Figure 5.** Effect of (a) the carbon chain length on ignition delay; (b) the magnitude of premixed combustion phase on thermal engine efficiency.

2.1.2 ETHERS COMPARED TO ALKANES

Fig. 5a shows that dipentyl ether (C10) had a 0.2 CAD shorter ignition delay than decane (C10). The shaft encoder resolution was 0.2 CAD and therefore this difference was deemed insignificant. It is interesting to note that dipentyl ether could perhaps be expected to have longer ignition delay than decane, based on the physical fuel properties of the two fuels: dipentyl ether has higher boiling point and surface tension values than decane (Appendix I) and could,
therefore, be expected to have poorer spray atomization and somewhat longer physical ignition delay. The fact that dipentyl ether and decane show similar values of ignition delay suggests that oxygen in the ether, which tends to shorten the ignition delay, offsets the opposing tendency of the physical properties. Considering first the chemistry of ether linkages, a laminar flow reactor study by Cai et al. \textsuperscript{36}, theoretical calculations of Ogura et al. \textsuperscript{37} and shock tube experiments of Guan et al. \textsuperscript{38} have shown that weakening in C-H bonds caused by the oxygen atom in an ether linkage result in faster H-abstraction from an ether, compared to that for a corresponding alkane. When considering the isomerization reactions that follow, Cai et al. \textsuperscript{36} observed that ethers can go through isomerization via hydrogen migration across the central oxygen atom. Additionally, the energy barrier of the peroxide decomposition, which will lead to further chain branching reactions, has been shown to be lower for ethers compared to the corresponding alkanes \textsuperscript{36,37}. Hence, it is suggested that due to the faster H-abstraction and higher ability of the fuel peroxy radical to undergo isomerization, the ignition chemistry of ethers is faster than that of the corresponding alkanes, but that the higher values of some physical fuel properties of ethers hinder the ignition of ether compared to the ignition of alkanes. This suggestion was supported by a previous study \textsuperscript{30}, which showed that dibutyl ether (C8) had a significantly shorter ignition delay than octane (C8), despite the higher boiling point, higher surface tension and higher viscosity of dibutyl ether.

2.1.3 VALERIC ESTER COMPARED TO KETONES AND ETHERS

Valeric esters have both a carbonyl group and an ether linkage in their structure as an ester group (Fig. 2). Fig. 5a shows that the ignition delays of valeric esters were higher than those of alkanes, ketones and the ether. Dayma et al. \textsuperscript{17} showed, by both modelling and experimentally in a jet stirred reactor, that the higher ignition delays of valeric esters compared to the corresponding
alkanes are caused mainly by the more difficult H-abstraction and the reduced ability of the fuel alkoxy peroxides to go through isomerization. The higher ignition delays of valeric esters compared to ketones or the ether are therefore partly explained by the differences in H-abstraction. As mentioned above, the H-abstraction from ethers is faster than from the corresponding alkanes but H-abstraction from ketones is slower than from the corresponding alkanes. When comparing the H-abstraction of ketones and esters, several studies have shown that the initial H-abstraction from a ketone occurs from the carbon atom next to the carbonyl group \(^{31-34}\); in the case of esters, H-abstraction is easiest from the carbon atom next to the ether oxygen \(^{17,39,40}\). The resulting ketone radical is more stable than the ester radical due to the presence of the ether oxygen in the ester group. Therefore, H-abstraction is easier from a ketone compared to an ester \(^{41}\). This is suggested to have, partly, caused the shorter ignition delays of ketones compared to esters observed in Fig. 5a.

When considering the isomerization of the fuel radical after H-abstraction, it was explained above that ethers may undergo isomerization more easily than the corresponding alkanes, but that the isomerization of molecules with a carbonyl group is more difficult than that of the corresponding alkanes. In the case of valeric esters, Dayma et al. \(^{17}\) suggested that the fuel radicals of valeric esters react with oxygen to form peroxy compounds. Most of these peroxy compounds react further through isomerization, but they can also form ethyl pentanoates by HO2 abstraction, hydroperoxides and oxygen through reaction with HO2, or alkoxy compounds by combining with other peroxides. In general, isomerization leads to fast formation of the radical pool and thus the ability of radicals of valeric esters to react through other routes than isomerization is considered to hinder the combustion of valeric esters. Additionally, several studies, e.g. Zhang and Boehman \(^{42}\), have stated that the ester moiety imposes extra strain on the
transition rings during isomerization, which may lower the rate of isomerization compared to the corresponding alkanes. It was suggested that the ester group may hinder the isomerization more than a carbonyl group and that this would delay further the ignition of esters, compared to ketones and ethers.

2.1.4 LEVULINATES COMPARED TO VALERIC ESTERS

Levulinates are 4-oxopentanoates with both a carbonyl group and an ester group, as shown in the molecular structures of ethyl levulinate and butyl levulinate in Fig. 2. Compared to valeric esters, levulinates have one more carbonyl group in their structure. It was observed from Fig. 5a that levulinates had the longest ignition delays of the tested molecules, slightly longer than the ignition delays of the corresponding valeric esters (longer by 0.23 CAD for C7 molecules and 0.28 CAD for C9 molecules). While the extra carbonyl group may contribute to the small increase in ignition delay over the delay for the esters, this small increase may also be explained, at least in part, by the higher boiling points and surface tension of levulinates (Appendix I) causing a potential deterioration in the injection fuel spray atomization.

When considering the chemical fuel properties, it was suggested that the addition of a carbonyl group to valeric ester to form a levulinate hindered the ignition in a similar way to that of adding a carbonyl group to an alkane to form a ketone; that is, H-abstraction becomes more difficult because the number of hydrogen atoms for H-abstraction is reduced by one and the C-H bonds close to the carbonyl group change, and the ability of a fuel peroxy radical to undergo isomerization is reduced. Interestingly, removing a carbonyl group from levulinate to form a valeric ester resulted in a significantly smaller decrease in ignition delay than when removing a carbonyl group from a ketone to form an alkane (Fig. 5a). This could potentially be explained by
greater decrease in the straight hydrocarbon chain length in the case of levulinates and valeric esters compared to the decrease for ketones and alkanes.

2.2 EFFECT OF MOLECULAR STRUCTURE ON ENGINE EFFICIENCY

Engine efficiency, which is defined as the conversion of fuel chemical energy to mechanical work, depends mainly on the air-fuel ratio and both the rate and timing of heat release from the fuel injected into the combustion chamber. The maximum engine efficiency is, in general, achieved with an Otto-cycle-like combustion, where most of the fuel burns rapidly in the premixed combustion mode at TDC. Too early combustion will decrease engine efficiency because high in-cylinder pressures are reached during the compression stroke. Similarly, too late combustion will reduce engine efficiency because part of the energy released will be rejected with the engine exhaust gases. Fig. 5b shows, as expected, positive correlations between engine efficiency and the quantity of fuel energy released during the premixed phase for all structural groups. Engine efficiency values of the molecules are presented in Appendix II. In the case of valeric esters, the unexpectedly high engine efficiency of pentyl valerate (49.1%) could be explained by the timing of the pHRR: pHRR was reached closer to TDC in pentyl valerate combustion (362.2 CAD), compared to the combustions of ethyl valerate (350.8 CAD) and butyl valerate (363.3 CAD) (Fig. 4). When all the data points are considered, however, there is no clear indication that a greater amount of premixed combustion has any considerable positive or negative influence on thermal engine efficiency. It should be noted, that valeric esters and the ether had similar, and ketones and levulinates lower, engine efficiency than the reference diesel (45.64%). When comparing the engine efficiencies of different molecular groups, however, it should be noted that the difference between several molecules were of the similar magnitude...
than the standard deviation of the mean efficiency of the reference diesel tests: 5-nonanone (41.3%) and nonane (41.4%); ethyl valerate (44%), ethyl levulinate (44.3%); ethyl levulinate (44.3%) and dipentyl ether (44.5%); pentyl valerate (49.1%) and heptane (49.4%). It should be said that the above observations are only tentative ones, because the values for efficiency shown in Fig. 5b are, on the whole, subject to considerable uncertainty, arising from the measurement of the fuel flow rate supplied to the engine combustion chamber. This involved measuring, (a) the flow rate supplied to the injector indirectly, from the movement of the enclosed UFVS piston, and (b) the fuel leakage rate from the injector; both there flow rates are very small and, individually, subject to considerable uncertainties; the net fuel flow rate to the combustion chamber, being the difference of these two small flow rates, is therefore subject to considerable error, which is expected to be reflected in the efficiency values shown in Fig. 5b.

2.3 EFFECTS OF FUEL MOLECULAR STRUCTURE ON EXHAUST GAS EMISSIONS

2.3.1 NITROGEN OXIDES

NOₓ emission formation in a compression ignition engine is affected by the fuel-bound oxygen, the global combustion temperature and availability of both oxygen and nitrogen from the air. It has been well established that the formation of NOₓ emissions is mainly temperature controlled and therefore significantly affected by the in-cylinder temperature. The combustion in-cylinder temperature, in turn, depends on the ignition delay, which affects the magnitude of the premixed combustion phase; in general, a longer ignition delay leads to a larger premixed phase releasing energy rapidly close to TDC, resulting in higher in-cylinder temperatures and greater formation of NOₓ.
Following on from this discussion in the previous paragraph, Fig. 6a and Fig. 6b show the expected positive correlations between NO$_x$ emission and both ignition delay and in-cylinder temperature for all molecular groups, excluding levulinates. The two levulinates show an opposing trend, which is suggested to occur due to the following reasons. Fig. 4 shows ethyl levulinate to stand out in having a prolonged cool combustion with very little energy released, followed by a late large premixed combustion phase. The prolonged period prior to energy release for the ethyl levulinate results in the heat release occurring later in the engine expansion stroke when cylinder volume has increased, compared to the other compounds, which causes a reduction in the overall premixed combustion temperature and thus also in NO$_x$ formation.
Figure 6. Changes in NO\textsubscript{x} emissions caused by (a) ignition delay, (b) in-cylinder temperature, (c) adiabatic flame temperature and (d) carbon chain length of the fuel molecule.
Fig. 6c shows NO<sub>x</sub> plotted against the adiabatic flame temperature, which was calculated according to the method presented by Turns<sup>24</sup>. Fig. 6c indicates a strong influence of adiabatic flame temperature on NO<sub>x</sub> emission, save for the case of the two levulinates, where the opposing trend may have been caused by the reasons discussed above in relation to Fig. 6a and Fig. 6b.

Fig. 6d shows the effect of the number of carbon atoms in the various fuel molecules on NO<sub>x</sub> emission. The results in this figure reflect to a significant extent the effect of ignition delay on NO<sub>x</sub> (Fig. 6a). Molecules with a greater number of carbon atoms tend to have shorter ignition delays, and hence lower NO<sub>x</sub> emission, than molecules with a lower number of carbon atoms for the reasons discussed previously in this paper. It can also be observed from Fig. 6d that the valeric esters have somewhat higher NO<sub>x</sub> emissions than the corresponding alkanes with the same number of carbon atoms. This appears to be related to the longer ignition delays of valeric esters compared to the alkanes, as can be seen in Fig. 6a. As a closing comment on Fig. 6, the number of data points for each molecular group is small (e.g. only two data points for ketones and levulinates) NO<sub>x</sub> trends discussed are, to a considerable extent, tentative ones.

2.3.2 PARTICULATE MATTER

Fig. 7 shows the results for particulate emissions. The trends in Fig. 7a for individual compounds are not conclusive: the particulate mass of alkanes and ketones reduced slowly with the increasing in-cylinder temperature, and this is likely to be due to the oxidation of already formed large agglomerates; however, the individual trends for the valeric esters and levulinates are not as expected (although the trend of levulinates might have been affected by the very late ignition of ethyl levulinate, shown in Fig. 4). When all the data points in Fig. 7a are taken together, there is a rather strong indication that higher in-cylinder temperature reduces the mass of particulates,
as one would expect. Fig. 7b shows that no clear correlation between the mass of particulates and
the number of carbon atoms in the various fuel molecules tested was observed. Likewise, Fig. 7c
also suggests that there was no clear influence on the number of particulates of the number of
carbon atoms in the molecules of the various tested compounds.

As in the case of the NO\textsubscript{x} trends discussed above, the trends for particulates are, to a
considerable extent, tentative ones due to the small number of data for individual molecular
groups.
Figure 7. Effect of (a) in-cylinder temperature and (b) carbon chain length on the mass of particulates; (c) effect of carbon chain length on the number of particulates in engine exhaust gas.
CONCLUSIONS

The compression ignition delays and exhaust gas emissions of several molecules, which, potentially, could be produced from lignocellulosic biomass were investigated. The tested molecules were levulinates, valeric esters, ketones, an ether and several alkanes. Ignition was ensured by testing each individual molecule with 30 wt-% heptane. The key results were as follows:

1. Ketones had longer ignition delays than alkanes because the carbonyl group makes H-abstraction more difficult from ketones, compared to alkanes, and also reduces the ability of the fuel peroxy radicals to undergo isomerization.

2. Dipentyl ether had a similar ignition delay to that of decane, despite the ether having an oxygen atom in its molecule embedded as an ether linkage. It is believed that the comparable delays occur because, in the case of the ester, physical properties (higher boiling point and higher surface tension) tend to increase the ignition delay while a chemical property (ether linkage) tends to reduce the ignition delay, with a result that both compounds end up with comparable ignition delay periods.

3. Valeric esters ignited later than ketones, ethers and alkanes. This was suggested to occur because the ester group results in more difficult H-abstraction and isomerization for valeric esters compares to ketones, ethers and alkanes.

4. Levulinates had slightly longer ignition delays compared to the corresponding valeric esters, most likely due to the additional carbonyl group in the structure of levulinates.

5. Valeric esters and the ether had similar engine efficiency than the reference diesel fuel.
6. Ketones and levulinates had slightly lower thermal engine efficiency than the reference diesel fuel.

7. NO\textsubscript{x} emissions appeared to be affected by both the in-cylinder temperatures than the adiabatic flame temperatures of the tested molecules.

8. NO\textsubscript{x} emissions of the oxygenated molecules were higher compared to those of alkanes and reference diesel fuel, but no consistent difference was observed between the NO\textsubscript{x} emissions of the oxygenated molecule groups.

9. The oxygenated molecules produced less of the heavy particulates but more of the light, smaller particulates compared to both alkanes and reference diesel fuel.

10. No real difference in the mass or the number of particulate emissions was observed between the structural groups tested.

11. As the tests were conducted at fixed injection timing, some of the variations in engine thermal efficiency and exhaust emissions are likely to have occurred due to variations in the timing of the combustion process relative to TDC, arising from variations in ignition delay.

As to be expected, the oxygen bearing molecules show a clear reduction in particulate mass, when compared with the non-oxygen bearing molecules and the fossil diesel fuel used as the reference test fuel. There is however, in the case of the oxygen bearing molecules a penalty in terms of an increase in the number of particulates (compared to reference diesel fuel and non-oxygenated molecules) which is particularly relevant due to recently introduced legislation to additional control the number of emitted particles for vehicle engines. The customary penalty of oxygen bearing molecules in terms of some increase in NO\textsubscript{x} can also be seen in the results presented in this paper. In terms of engine thermal efficiency, some of the oxygen bearing
molecules, especially the levulinates, have shown efficiency levels similar to those of the non-oxygen bearing molecules. It should be noted, however, that some of the trends discussed in the paper are, to a considerable extent, only tentative and more data are necessary before firm conclusions could be drawn. Nevertheless, there is considerable evidence from the results that the oxygen bearing compounds tested, which could potentially be obtained from lignocellulosic materials, can potentially be used as diesel fuel extenders and would warrant further detailed investigations, including tests in diesel-engine vehicles.

APPENDIX I

Physical properties of the tested fuel molecules [23]

<table>
<thead>
<tr>
<th>Fuel molecule</th>
<th>Boiling point (K)</th>
<th>Density at 298 K [g/ml]</th>
<th>Surface tension at 298 K [N/m]</th>
<th>Dynamic Viscosity at 298 K [Pa*s]</th>
<th>Lower heating value [MJ/kg]</th>
<th>C/H Atomic ratio</th>
<th>O (m %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>372</td>
<td>0.682</td>
<td>0.0198</td>
<td>0.00039</td>
<td>45</td>
<td>0.448</td>
<td>0</td>
</tr>
<tr>
<td>Nonane</td>
<td>424</td>
<td>0.715</td>
<td>0.0224</td>
<td>0.00067</td>
<td>45</td>
<td>0.450</td>
<td>0</td>
</tr>
<tr>
<td>Decane</td>
<td>447</td>
<td>0.73</td>
<td>0.0234</td>
<td>0.00086</td>
<td>44</td>
<td>0.455</td>
<td>0</td>
</tr>
<tr>
<td><strong>Ether</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipentyl ether</td>
<td>460</td>
<td>0.785</td>
<td>0.0243</td>
<td>0.00161</td>
<td>39</td>
<td>0.455</td>
<td>10.1</td>
</tr>
<tr>
<td><strong>Ketone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Heptanone</td>
<td>421</td>
<td>0.818</td>
<td>0.0261</td>
<td>0.00075</td>
<td>36</td>
<td>0.5</td>
<td>14.0</td>
</tr>
<tr>
<td>5-Nonanone</td>
<td>462.6</td>
<td>0.826</td>
<td>0.0265</td>
<td>Not available</td>
<td>38</td>
<td>0.5</td>
<td>11.3</td>
</tr>
<tr>
<td><strong>Levulinate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl levulinate</td>
<td>480</td>
<td>1.016</td>
<td>0.0307</td>
<td>Not available</td>
<td>24</td>
<td>0.58</td>
<td>33.3</td>
</tr>
<tr>
<td>Butyl levulinate</td>
<td>514</td>
<td>0.974</td>
<td>0.0312</td>
<td>Not available</td>
<td>28</td>
<td>0.56</td>
<td>27.9</td>
</tr>
<tr>
<td><strong>Valerate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl valerate</td>
<td>420</td>
<td>0.875</td>
<td>0.0267</td>
<td>0.00847 [26]</td>
<td>31</td>
<td>0.5</td>
<td>24.6</td>
</tr>
<tr>
<td>Butyl valerate</td>
<td>462</td>
<td>0.868</td>
<td>0.0279</td>
<td>Not available</td>
<td>33</td>
<td>0.5</td>
<td>20.3</td>
</tr>
<tr>
<td>Pentyl valerate</td>
<td>481</td>
<td>0.865</td>
<td>0.0283</td>
<td>Not available</td>
<td>34</td>
<td>0.5</td>
<td>18.6</td>
</tr>
</tbody>
</table>
APPENDIX II

Results of the combustion experiments

<table>
<thead>
<tr>
<th>Fuel molecule</th>
<th>Ignition delay (CAD)</th>
<th>Premixed phase (%)</th>
<th>Maximum average in-cylinder temperature (K)</th>
<th>Peak HRR (J/CAD)</th>
<th>Timing of Peak HRR (CAD)</th>
<th>Engine efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptane</td>
<td>5.3</td>
<td>25.7</td>
<td>1481</td>
<td>65.0</td>
<td>359.4</td>
<td>49.4</td>
</tr>
<tr>
<td>Nonane</td>
<td>5.1</td>
<td>23.0</td>
<td>1450</td>
<td>60.5</td>
<td>359.5</td>
<td>41.4</td>
</tr>
<tr>
<td>Decane</td>
<td>4.7</td>
<td>21.2</td>
<td>1453</td>
<td>52.4</td>
<td>358.8</td>
<td>40.9</td>
</tr>
<tr>
<td><strong>Ether</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipentyl ether</td>
<td>4.5</td>
<td>45.8</td>
<td>1476</td>
<td>46.0</td>
<td>361.6</td>
<td>44.5</td>
</tr>
<tr>
<td><strong>Ketone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Heptanone</td>
<td>6.9</td>
<td>40.8</td>
<td>1506</td>
<td>167.6</td>
<td>363.7</td>
<td>28.5</td>
</tr>
<tr>
<td>5-Nonanone</td>
<td>5.9</td>
<td>48.9</td>
<td>1467</td>
<td>131.0</td>
<td>361.1</td>
<td>41.3</td>
</tr>
<tr>
<td><strong>Levulinate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl levulinate</td>
<td>8.0</td>
<td>80.8</td>
<td>1548</td>
<td>132.4</td>
<td>367.5</td>
<td>44.3</td>
</tr>
<tr>
<td>Butyl levulinate</td>
<td>7.4</td>
<td>51.3</td>
<td>1516</td>
<td>177.4</td>
<td>364.7</td>
<td>33.7</td>
</tr>
<tr>
<td><strong>Valerate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl valerate</td>
<td>7.8</td>
<td>63.0</td>
<td>1529</td>
<td>168.0</td>
<td>365.6</td>
<td>44.0</td>
</tr>
<tr>
<td>Butyl valerate</td>
<td>7.2</td>
<td>70.4</td>
<td>1502</td>
<td>165.6</td>
<td>363.3</td>
<td>47.9</td>
</tr>
<tr>
<td>Pentyl valerate</td>
<td>6.6</td>
<td>62.5</td>
<td>1496</td>
<td>152.2</td>
<td>362.2</td>
<td>49.1</td>
</tr>
<tr>
<td><strong>Reference</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>5.7</td>
<td>51.6</td>
<td>1501</td>
<td>132.2</td>
<td>361.1</td>
<td>45.6</td>
</tr>
</tbody>
</table>

AUTHOR INFORMATION

Corresponding Author

* Elina Koivisto * Address; Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom; E-mail addresses:
elina.koivisto.11@ucl.ac.uk, elina.koivisto3@gmail.com; Tel: +44 (0)20 7679 3907; Fax: +44(0)20 7679 0180
Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

ACKNOWLEDGMENT

The authors would like to thank BP plc. for technical and financial support.

ABBREVIATIONS

FAME, Fatty acid methyl esters; CAD, crank angle degrees; TDC, top dead center; NOₓ, nitrogen oxides; CO, carbon monoxide; NDIR, non-dispersive infrared; CO₂, carbon dioxide; O₂, oxygen; IMEP, indicated mean effective pressure; wt-%, weight percentage; v%, volume percentage.

REFERENCES


Yanowitz J, Ratcliff MA, McCormick RL, Taylor JD, Murphy MJ. Compendium of Experimental Cetane Numbers.; 2014.


Molecules Effects on diesel combustion of the molecular structure of potential synthetic bio-fuel molecules.; SAE Tech Pap 242007.


