- ¹ The compression ignition and exhaust gas emissions
- ² of fuel molecules which can be produced from
- ³ lignocellulosic biomass: levulinates, valeric esters

4 and ketones

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- 16 particulate emissions

17 ABSTRACT

18 This paper presents the results of combustion experiments conducted in a single cylinder 19 compression ignition engine with several fuel molecules which can be produced from 20 lignocellulosic biomass through a variety of processing routes. The lignocellulosic fuel 21 molecules tested were ethyl levulinate, butyl levulinate, ethyl valerate, butyl valerate, pentyl 22 valerate, 5-nonanone, 3-heptanone, dipentyl ether and three alkanes. To ensure reliable 23 compression ignition of all of the molecules, all of the molecules were tested after adding 30 wt-24 % of heptane to them. Levulinates were observed to have longer ignition delays than valeric 25 esters, which in turn had longer ignition delays compared to ketones. All of the tested 26 oxygenated molecules ignited later than the corresponding alkanes, excluding dipentyl ether. The 27 differences in ignition delays where mainly attributed to the higher electronegativity of oxygen 28 atoms compared to that of carbon and hydrogen atoms. The tested molecules, excluding 3-29 heptanone, had similar engine efficiency than to that of diesel fuel. However, the oxygenated 30 fuel molecules resulted in higher NOx emissions and higher number of small particulates in 31 exhaust gas emissions compared to alkanes and diesel fuel.

32 INTRODUCTION

33 Fuels made from lignocellulosic biomass are potential second generation biofuels. 34 Lignocellulose includes the most abundant polymers on Earth and it is not likely to be a human 35 food source¹. Lignocellulosic biomass includes agricultural and forestry residues, herbaceous 36 energy crops and it can be found in municipal solid waste. However, breaking the strong 37 structure of lignocellulose and converting it to biofuel molecules involves rather complicated 38 processes. The relative difficulty in developing commercially feasible technologies to do this is 39 the main reason why lignocellulosic biofuels are not currently widely produced until recently 2 . 40 For example, the world's first wood-based renewable commercial fuel production started 41 commercial operation in UPM Lappeenranta Biorefinery in Finland in January 2015³.

42 Lignocellulosic biomass can be converted into biofuels through thermal, biological and catalytic
43 routes. The catalytic approach can be used to produce furfurals from lignocellulose through acid

44 hydrolysis. The furfurals can, in turn, be converted into several chemicals, polymers, bioalcohols 45 (e.g. ethanol), gasoline octane busters (e.g. 2-methylfuran and dimethylfuran) and levulinic acid. 46 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 47 lignocellulose in large scale is ongoing: several possible pathways were described in the review 48 articles by Rackemann and Doherty⁴ and Deng et al.⁵. Biofuel molecules such as 2-methylfuran, 49 γ -Valerolactone, valeric esters and levulinates can be produced from levulinic acid¹. A general 50 chemical route to produce these biofuel molecules from lignocellulosic material is shown in Fig. 51 1⁶. Because esters are known to be viable biofuels for diesel engines ⁷⁻⁹, this study focused on 52 53 the combustion of levulinates as well as valeric esters.



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Figure 1. Production of levulinates and valeric esters from C6 sugars of lignocellulosic materials
 (adapted from [6]).

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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. ¹⁰ The low cetane numbers of levulinates limit their blend proportion in diesel blends ¹¹. According to Joshi et al. ¹², diesel

66 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 67 Donnelly ¹³ concluded that butyl levulinate is a poor alternative for aviation kerosene because it 68 69 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.¹⁴, only a small 70 71 number of kinetic studies and engine studies are available on the oxidation of alkyl levulinates. Christensen et al.¹⁰ tested ethyl levulinate and butyl levulinate as diesel blends in a 2008 model 72 73 year Cummins ISB engine. With 10 v% ethyl levulinate and 20 v% butyl levulinate blends they 74 observed no change in total hydrocarbon, CO, or particulate matter exhaust gas emissions. The 75 engine-out smoke number was reduced by 41.3% and 55%, respective of the two blends, while NO_x emissions were observed to increase by 0% and 4.6%, respectively. Janssen et al. ¹⁵ 76 conducted experiments of 60, 70 and 80 v% butyl levulinate/tetradecane blends in a single 77 78 cylinder research engine. They observed that a reduction up to 95% (depending on the load) in 79 particulate emissions could be achieved with butyl levulinate addition to tetradecane, compared 80 to fossil diesel fuel. However, an increase was observed in hydrocarbon, CO and noise emissions 81 for butyl levulinate/tetradecane blends compared to fossil diesel fuel. Nevertheless, Christensen et al. ¹⁰ concluded that commercial applications of levulinates would be challenging due to their 82 83 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 ^{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 ¹⁶. According to Lange et al. ¹⁶, 20 v% of ethyl valerate in gasoline meets the

89 research and motor octane numbers of European gasoline specification (EN 228), whereas butyl 90 valerates and higher valeric esters could be suitable for diesel blends. Lange et al. ¹⁶ reported that 91 blends of pentyl valerate and diesel have higher volatility, compared to fatty acid methyl esters 92 (FAME), and that blending pentyl valerate with diesel improved cold flow properties more than 93 blends of FAME, although FAME also has a lower cetane number. Very few studies have 94 investigated the combustion kinetics and engine combustion of valerates and levulinates, and in 95 the case of valerates such studies are particularity scarce. Research on the oxidation of ethyl or 96 higher esters is generally scarce, mainly because methyl esters are the dominant compounds of 97 current biodiesel fuels and, therefore, currently a main research focus. Combustion kinetic schemes for ethyl valerate and butyl valerate have been proposed by Davma et al.¹⁷, while 98 Contino et al.¹⁸ investigated the combustion of butyl and pentyl valerates in a single cylinder 99 PSA DW10 engine. Contino et al.¹⁸ concluded that, compared to diesel fuel, neither 20 v% of 100 101 butyl valerate or 20 v% pentyl valerate added to diesel fuel resulted in significant changes in 102 exhaust gas emissions or engine performance, despite an increase in ignition delay.

103 In the study reported here two levulinates, three valeric esters, two ketones, an ether and three 104 alkanes were tested in a single cylinder diesel research engine with the aim of improving the 105 understanding of their combustion characteristics, especially the ignition delay, and exhaust gas 106 emissions of these potential lignocellulose-driven fuel molecules. Ketones, namely 3-heptanone 107 and 5-nonanone, were tested because valeric acid, which can be esterified to produce valeric 108 esters, can also be ketonized to form 5-nonanone and the 5-nonanone can subsequently be 109 upgraded into several different hydrocarbons (such as straight chain alkanes and their isomers) 110 using an acid catalyst ¹. These hydrocarbons include straight chain alkanes (e.g. nonane), and for 111 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.

119 1. EXPERIMENTAL METHODS

120 1.1 ENGINE

121 The tests were conducted on a direct injection compression ignition research engine, which was 122 naturally aspirated. The engine parameters are listed in Table 1. The single-cylinder research 123 engine was constructed with parts from a donor Ford Duratorq commercial engine (engine head, 124 piston, connecting rod, and injector), so major aspects of the combustion and fuel injector 125 systems were identical to those of the commercial engine. The cylinder gas pressure was 126 measured by means of a piezoelectric transducer (Kistler 6056AU38), located in an engine glow 127 plug adapter, and a charge amplifier (Kistler 5011). A piezo resistive pressure transducer (Druck 128 PTX 7517-3257), located in the engine intake manifold 160 mm upstream of the intake valve, 129 was used to detect a reference absolute pressure once per engine cycle at bottom dead center. 130 The absolute pressure was used to provide an absolute pressure reference every cycle for the 131 piezoelectric transducer pressure record. The cylinder pressure from the piezoelectric transducer 132 was digitized every 0.2 crank angle degrees (CAD) by a data acquisition system, which was 133 controlled by a shaft encoder which provided digitization trigger every 0.2 CAD and a cycle 134 reference signal at top dead center (TDC). The digitized pressure records for one hundred

- 135 consecutive engine cycles were then averaged and this ensemble average pressure record at 0.2
- 136 CAD intervals was used for thermodynamic heat release rate analysis.
- 137

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

138 **Table 1.** Spesifications of the naturally aspirated research engine.

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140 Because some of the tested fuel molecules had limited availability and high purchase costs, an 141 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 142 143 conventional common rail fuel injection system and, instead, it operates as a separate low 144 volume fuel injection system, supplying the engine fuel injector directly. However, although it 145 dispenses of the conventional common rail system as a fuel injection system, it still utilizes the 146 common rail system but only as a high pressure, highly controllable, hydraulic system to 147 pressurize the UFVS. A typical test, using for example 200ml of sample fuel, would commence 148 with the engine coolant and oil fully warmed up and the engine being motored for a while at test 149 speed until various temperatures around the engine, including coolant and oil stabilized. Injection 150 from the UFVS would then commence and maintained for a period of a few minutes until the 151 engine IMEP and exhaust emissions have stabilized, after which data was collected for at least 152 100 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.

160 1.2 ANALYSIS OF EXHAUST GAS EMISSIONS

161 The engine exhaust gas was sampled 180 mm downstream of the exhaust valves and led through 162 a heated line to two gas analyzers. The total mass and number of particles per unit volume as 163 well as the particle size distribution of the exhaust gas sample was measured with a Cambustion 164 DMS 500 differential mobility spectrometer system. A particle density of 1.77 g/cm³ was 165 assumed ²². A frequently calibrated MEXA 9100HEGR emission analysis system measured the 166 concentrations of nitrogen oxides (NO_x) by chemiluminescence, carbon monoxide (CO) by non-167 dispersive infrared (NDIR), carbon dioxide (CO_2) by NDIR, oxygen (O_2) by paramagnetic 168 detector, and unburned hydrocarbons by flame ionization in the exhaust gas sample.

169 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 175 changes or day-to-day drifts in the equipment or the instrumentation. Based on this log with 176 reference diesel fuel, the long term mean value of the NO_x emission was 807.24 ppm, the 177 standard deviation of the mean NO_x was 44.7 ppm and standard error of the mean 5.53 ppm. The 178 corresponding values for the mass of particulate matter in the engine exhaust gas were 0.0081 179 μ g/cc, 0.0013 μ g/cc and 0.00066 μ g/cc; and for the numbers of particulates in the engine exhaust 180 gas they were 8.85*10⁷ N/cc, 3.90*10⁷ N/cc and 1.95*10⁷ N/cc, respectively.

181 1.4 DATA ANALYSIS

182 The heat release rate (HRR) used in the data analysis was the net heat release rate, which was 183 considered as the difference between: chemical energy released to the engine cylinder contents 184 by combustion minus the heat transfer from the engine cylinder contents to the combustion chamber surfaces, as shown in Heywood ²³. The engine in-cylinder contents were assumed to be 185 186 at uniform pressure and temperature and were modelled as an ideal gas. The percentage of the 187 fuel that burned during the premixing controlled phase, denoted as premixed phase, was 188 calculated as the ratio of: the cumulative HRR that occurred between SOC and the end of the 189 premixed phase divided by the measured chemical fuel energy injected during the engine cycle. 190 The end of the premixed phase was defined as the highest maximum value of the second 191 derivative of HRR. The adiabatic flame temperature at constant pressure was calculated from 192 iteration of the absolute enthalpy of the reactants at the initial in-cylinder temperature and that of 193 the products at the adiabatic flame temperature. The iteration was conducted as presented by Turns²⁴. In the case of heptane blends, the heptane in the mixture was taken into account when 194 195 calculating the adiabatic flame temperatures of the blends. Engine efficiency was considered as 196 the indicated engine thermal efficiency, which was calculated as a ratio of: the indicated work 197 output of the engine divided by the fuel chemical energy supplied to the engine during one

198 engine cycle. The reproducibility of the efficiency measurements was evaluated as described in 199 section 1.3, above. Based on the set of 26 repeated tests with the reference diesel fuel, the long 200 term mean value of the engine thermal efficiency was 45.6 %, the standard deviation of the mean 201 value of the efficiency was 0.33% (percentage points) and standard error of the mean value of 202 the efficiency was 0.065% (percentage points). The maximum average in-cylinder temperature, 203 also known as global gas temperature, was calculated from the instantaneous in-cylinder 204 temperature, which was calculated for any given time using the ideal gas law. The number of air 205 moles present in the engine cylinder was estimated from the measurement of the air flow rate 206 supplied to the engine. The values of in-cylinder temperature for hundred consecutive engine 207 cycles were averaged for the calculation of net heat release rate and of the maximum average in-208 cylinder temperature.

209 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.



Figure 2. Tested molecule sets.

221 Initially, ethyl levulinate, butyl levulinate, ethyl valerate and butyl valerate were tested each one 222 on its own, as pure compounds, and none of these fuel molecules were observed to ignite in the 223 diesel engine. Therefore, in order to enable reliable ignition, heptane was added to all the tested 224 molecules. Heptane was selected as the ignition improver due to its similar combustion qualities 225 compared to fossil diesel fuel. The amount of heptane added was the same (m %) for all 226 molecules to allow comparison between the combustion chemistries of the molecules. The 227 quantity of heptane in the blends was decided after further tests were conducted with ethyl 228 levulinate, because it had the shortest carbon chain length and the highest oxygen content of the 229 tested molecules; therefore, it was the most difficult molecule to ignite. Mixtures with 20, 30 and

230 40 wt-% added heptane by mass were tried. It was found that 30 wt-% of heptane was the 231 smallest amount of heptane that could be added to ethyl levulinate for reliable ignition, without a 232 pronounced two-stage ignition. To allow the results from all the fuel molecules tested to be 233 readily compared, 30 wt-% of heptane was added to all of the investigated molecules. The effect 234 of heptane on the combustion chemistry of the fuel mixtures is assumed to be similar in each test 235 for the purposes of this study, because the same amount (m %) of heptane was added to each one 236 of the molecules. Heptane interacts with the combustion of the molecules by donating radicals to 237 the combustion mixture and, due to the same amount of heptane in the mixture, similar amounts 238 of radicals from heptane may be expected to be available for each molecule at any given 239 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.
- 243 2. Adding an ether linkage to an alkane to form an ether
- 244
 25 3. Combining a carbonyl group and an ether linkage into an ester group to form a valeric
 245 ester
- 4. Adding a carbonyl group to the valeric ester to form a levulinate
- 247
- 248 2. RESULTS AND DISCUSSION
- 249 2.1 EFFECT OF MOLECULAR STRUCTURE ON IGNITION DELAY

250 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

252 premixed-combustion mode. Fig. 3a shows, as expected, a positive correlation between the 253 amount of premixed phase and ignition delay for alkanes and levulinates. Interestingly, ketones 254 had a negative correlation and valeric esters no correlation between premixed phase and ignition 255 delay when the premixed phase quantity was calculated as a percentage of energy injected, 256 where the energy injected was defined as the chemical energy of the fuel injected during an 257 engine cycle (Fig. 3a). The data presented in Fig. 3 is listed for each molecule in Appendix II. It 258 is suggested, that the unexpectedly small premixed phases of the ketone 3-heptanone and the 259 ethyl valerate (Fig. 3a) were caused by their lower percentages of total fuel combusted, 260 compared to those of the other molecules in the same structural group. The lower combustion 261 percentages resulted from the more difficult ignition of these molecules; for example, in the case 262 of 3-heptanone only 61% of all the fuel energy was released during combustion, compared to the 263 corresponding value of 89% for 5-nonanone. In the case of ethyl valerate only 90% of all the 264 injected fuel energy was released during combustion, compared to the 99% for both butyl and 265 pentyl valerate. It should be noted, that although the correlation between the ignition delay and 266 premixed percentage within the structural groups was not positive for all the compounds (as one 267 would expect), Fig. 3a shows that taken together, the data points for all compounds tested show a 268 quite clear trend for the percentage of premixed combustion to increase when ignition delay 269 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.

275 Longer ignition delay was generally observed to result in higher in-cylinder temperature (Fig. 276 3b), higher peak HRR (Fig. 3c) and later timing of the peak HRR (Fig. 3d), as was expected. An 277 exception to these trends was the levulinates, which did not show a rising peak HRR with 278 increasing ignition delay (Fig. 3c). The lower peak HRR of ethyl levulinate compared to that of 279 butyl levulinate (Fig. 3c) may be explained by the peak HRR occurring later in the expansion 280 stroke for ethyl levulinate, as shown in Fig. 4 (see also Appendix II), where the combustion 281 volume is greater. Nevertheless, despite combustion in a larger volume, ethyl valerate can be 282 seen from Fig. 3b to reach a higher average combustion temperature. This can be explained by 283 the substantially larger amount of premixed combustion of ethyl valerate (Fig. 3a).

284



igure 4. Heat release rates of the tested molecules.

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288 2.1.1 KETONES COMPARED TO ALKANES

289 The effect of adding a carbonyl group to an alkane to form a ketone was investigated by 290 comparing 3-heptanone to heptane and 5-nonanone to nonane. Fig. 5a shows that ketones had 291 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 292 293 delays than the corresponding alkanes. The later ignition of ketones, compared to alkanes, was 294 suggested to be mainly caused by the oxygen atom in the carbonyl group of ketones. The 295 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} 296 297 have shown that the higher electronegativity of an oxygen atom, compared to that of carbon and 298 hydrogen atoms, affects the strength of carbon-hydrogen bonds near the oxygen atom: the 299 strength of the carbon-hydrogen bonds on the carbons next to the carbonyl group is weakened, 300 but the strength of the carbon-hydrogen bonds on the next three carbon atoms of the chain are 301 increased. Oxygen atom in the carbonyl group makes the overall H-abstraction from the 302 oxygenated molecule more difficult than H-abstraction from the corresponding alkane 303 molecules, thus increasing the ignition delay. In the case of isomerization, the rapid compression 304 machine studies of Allen et al.³⁵ have showed that carbonyl group hinders the formation of a 305 transition ring during isomerization, compared to an alkane, and thus increases the ignition delay 306 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, 307 308 instead of branching reactions through isomerization. This will contribute to the slower 309 formation of a radical pool large enough to initiate and sustain ignition in the case of ketones 310 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.

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317 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, 323 therefore, be expected to have poorer spray atomization and somewhat longer physical ignition 324 delay. The fact that dipentyl ether and decane show similar values of ignition delay suggests that 325 oxygen in the ether, which tends to shorten the ignition delay, offsets the opposing tendency of 326 the physical properties. Considering first the chemistry of ether linkages, a laminar flow reactor 327 study by Cai et al. ³⁶, theoretical calculations of Ogura et al. ³⁷ and shock tube experiments of Guan et al. ³⁸ have shown that weakening in C-H bonds caused by the oxygen atom in an ether 328 329 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. ³⁶ observed that ethers can 330 331 go through isomerization via hydrogen migration across the central oxygen atom. Additionally, 332 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 ^{36,37}. 333 334 Hence, it is suggested that due to the faster H-abstraction and higher ability of the fuel peroxy 335 radical to undergo isomerization, the ignition chemistry of ethers is faster than that of the 336 corresponding alkanes, but that the higher values of some physical fuel properties of ethers 337 hinder the ignition of ether compared to the ignition of alkanes. This suggestion was supported by a previous study ³⁰, which showed that dibutyl ether (C8) had a significantly shorter ignition 338 339 delay than octane (C8), despite the higher boiling point, higher surface tension and higher 340 viscosity of dibutyl ether.

341 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. ¹⁷ showed, by both modelling and experimentally in a jet stirred reactor, that the higher ignition delays of valeric esters compared to the corresponding 346 alkanes are caused mainly by the more difficult H-abstraction and the reduced ability of the fuel 347 alkoxy peroxides to go through isomerization. The higher ignition delays of valeric esters 348 compared to ketones or the ether are therefore partly explained by the differences in H-349 abstraction. As mentioned above, the H-abstraction from ethers is faster than from the 350 corresponding alkanes but H-abstraction from ketones is slower than from the corresponding 351 alkanes. When comparing the H-abstraction of ketones and esters, several studies have shown 352 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 353 oxygen ^{17,39,40}. The resulting ketone radical is more stable than the ester radical due to the 354 355 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 356 357 ketones compared to esters observed in Fig. 5a.

358 When considering the isomerization of the fuel radical after H-abstraction, it was explained 359 above that ethers may undergo isomerization more easily than the corresponding alkanes, but 360 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 361 362 radicals of valeric esters react with oxygen to form peroxy compounds. Most of these peroxy 363 compounds react further through isomerization, but they can also form ethyl pentanoates by HO2 364 abstraction, hydroperoxides and oxygen through reaction with HO2, or alkoxy compounds by 365 combining with other peroxides. In general, isomerization leads to fast formation of the radical 366 pool and thus the ability of radicals of valeric esters to react through other routes than 367 isomerization is considered to hinder the combustion of valeric esters. Additionally, several studies, e.g. Zhang and Boehman⁴², have stated that the ester moiety imposes extra strain on the 368

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.

373 2.1.4 LEVULINATES COMPARED TO VALERIC ESTERS

374 Levulinates are 4-oxopentanoates with both a carbonyl group and an ester group, as shown in the 375 molecular structures of ethyl levulinate and butyl levulinate in Fig. 2. Compared to valeric esters, 376 levulinates have one more carbonyl group in their structure. It was observed from Fig. 5a that 377 levulinates had the longest ignition delays of the tested molecules, slightly longer than the 378 ignition delays of the corresponding valeric esters (longer by 0.23 CAD for C7 molecules and 379 0.28 CAD for C9 molecules). While the extra carbonyl group may contribute to the small 380 increase in ignition delay over the delay for the esters, this small increase may also be explained, 381 at least in part, by the higher boiling points and surface tension of levulinates (Appendix I) 382 causing a potential deterioration in the injection fuel spray atomization.

383 When considering the chemical fuel properties, it was suggested that the addition of a carbonyl 384 group to valeric ester to form a levulinate hindered the ignition in a similar way to that of adding 385 a carbonyl group to an alkane to form a ketone; that is, H-abstraction becomes more difficult 386 because the number of hydrogen atoms for H-abstraction is reduced by one and the C-H bonds 387 close to the carbonyl group change, and the ability of a fuel peroxy radical to undergo 388 isomerization is reduced. Interestingly, removing a carbonyl group from levulinate to form a 389 valeric ester resulted in a significantly smaller decrease in ignition delay than when removing a 390 carbonyl group from a ketone to form an alkane (Fig. 5a). This could potentially be explained by

391 greater decrease in the straight hydrocarbon chain length in the case of levulinates and valeric392 esters compared to the decrease for ketones and alkanes.

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394 2.2 EFFECT OF MOLECULAR STRUCTURE ON ENGINE EFFICIENCY

395 Engine efficiency, which is defined as the conversion of fuel chemical energy to mechanical 396 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 ²³. The maximum engine efficiency is, in general, 397 398 achieved with an Otto-cycle-like combustion, where most of the fuel burns rapidly in the 399 premixed combustion mode at TDC. Too early combustion will decrease engine efficiency 400 because high in-cylinder pressures are reached during the compression stroke. Similarly, too late 401 combustion will reduce engine efficiency because part of the energy released will be rejected 402 with the engine exhaust gases. Fig. 5b shows, as expected, positive correlations between engine 403 efficiency and the quantity of fuel energy released during the premixed phase for all structural 404 groups. Engine efficiency values of the molecules are presented in Appendix II. In the case of 405 valeric esters, the unexpectedly high engine efficiency of pentyl valerate (49.1%) could be 406 explained by the timing of the pHRR: pHRR was reached closer to TDC in pentyl valerate 407 combustion (362.2 CAD), compared to the combustions of ethyl valerate (350.8 CAD) and butyl 408 valerate (363.3 CAD) (Fig. 4). When all the data points are considered, however, there is no 409 clear indication that a greater amount of premixed combustion has any considerable positive or 410 negative influence on thermal engine efficiency. It should be noted, that valeric esters and the 411 ether had similar, and ketones and levulinates lower, engine efficiency than the reference diesel 412 (45.64%). When comparing the engine efficiencies of different molecular groups, however, it 413 should be noted that the difference between several molecules were of the similar magnitude

414 than the standard deviation of the mean efficiency of the reference diesel tests: 5-nonanone 415 (41.3%) and nonane (41.4%); ethyl valerate (44%), ethyl levulinate (44.3%); ethyl levulinate 416 (44.3%) and dipentyl ether (44.5%); pentyl valerate (49.1%) and heptane (49.4%). It should be 417 said that the above observations are only tentative ones, because the values for efficiency shown 418 in Fig. 5b are, on the whole, subject to considerable uncertainty, arising from the measurement of 419 the fuel flow rate supplied to the engine combustion chamber. This involved measuring, (a) the 420 flow rate supplied to the injector indirectly, from the movement of the enclosed UFVS piston, 421 and (b) the fuel leakage rate from the injector; both there flow rates are very small and, 422 individually, subject to considerable uncertainties; the net fuel flow rate to the combustion 423 chamber, being the difference of these two small flow rates, is therefore subject to considerable 424 error, which is expected to be reflected in the efficiency values shown in Fig. 5b.

425

426 2.3 EFFECTS OF FUEL MOLECULAR STRUCTURE ON EXHAUST GAS EMISSIONS427 2.3.1 NITROGEN OXIDES

NO_x emission formation in a compression ignition engine is affected by the fuel-bound oxygen, 428 429 the global combustion temperature and availability of both oxygen and nitrogen from the air. It 430 has been well established that the formation of NO_x emissions is mainly temperature controlled 431 ^{23,43,44} and therefore significantly affected by the in-cylinder temperature. The combustion in-432 cylinder temperature, in turn, depends on the ignition delay, which affects the magnitude of the 433 premixed combustion phase; in general, a longer ignition delay leads to a larger premixed phase 434 releasing energy rapidly close to TDC, resulting in higher in-cylinder temperatures and greater 435 formation of NO_x.

436 Following on from this discussion in the previous paragraph, Fig. 6a and Fig. 6b show the 437 expected positive correlations between NO_x emission and both ignition delay and in-cylinder 438 temperature for all molecular groups, excluding levulinates. The two levulinates show an 439 opposing trend, which is suggested to occur due to the following reasons. Fig. 4 shows ethyl 440 levulinate to stand out in having a prolonged cool combustion with very little energy released, 441 followed by a late large premixed combustion phase. The prolonged period prior to energy 442 release for the ethyl levulinate results in the heat release occurring later in the engine expansion 443 stroke when cylinder volume has increased, compared to the other compounds, which causes a 444 reduction in the overall premixed combustion temperature and thus also in NO_x formation.





447 Figure 6. Changes in NO_x emissions caused by (a) ignition delay, (b) in-cylinder temperature,
448 (c) adiabatic flame temperature and (d) carbon chain length of the fuel molecule.

450 Fig. 6c shows NO_x plotted against the adiabatic flame temperature, which was calculated 451 according to the method presented by Turns ²⁴. Fig. 6c indicates a strong influence of adiabatic

452 flame temperature on NO_x emission, save for the case of the two levulinates, where the opposing 453 trend may have been caused by the reasons discussed above in relation to Fig. 6a and Fig. 6b.

454 Fig. 6d shows the effect of the number of carbon atoms in the various fuel molecules on NO_x 455 emission. The results in this figure reflect to a significant extent the effect of ignition delay on 456 NO_x (Fig. 6a). Molecules with a greater number of carbon atoms tend to have shorter ignition 457 delays, and hence lower NO_x emission, than molecules with a lower number of carbon atoms for 458 the reasons discussed previously in this paper. It can also be observed from Fig. 6d that the 459 valeric esters have somewhat higher NOx emissions than the corresponding alkanes with the 460 same number of carbon atoms. This appears to be related to the longer ignition delays of valeric 461 esters compared to the alkanes, as can be seen in Fig. 6a. As a closing comment on Fig. 6, the 462 number of data points for each molecular group is small (e.g. only two data points for ketones 463 and levulinates) NO_x trends discussed are, to a considerable extent, tentative ones.

464 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.

476 As in the case of the NO_x trends discussed above, the trends for particulates are, to a 477 considerable extent, tentative ones due to the small number of data for individual molecular 478 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.

486 487

3.

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:

493
1. Ketones had longer ignition delays than alkanes because the carbonyl group makes H494 abstraction more difficult from ketones, compared to alkanes, and also reduces the
495 ability of the fuel peroxy radicals to undergo isomerization.

- 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
- 502 3. Valeric esters ignited later than ketones, ethers and alkanes. This was suggested to
 503 occur because the ester group results in more difficult H-abstraction and
 504 isomerization for valeric esters compares to ketones, ethers and alkanes.
- 505
 4. Levulinates had slightly longer ignition delays compared to the corresponding valeric
 506
 esters, most likely due to the additional carbonyl group in the structure of levulinates.
- 507 5. Valeric esters and the ether had similar engine efficiency than the reference diesel508 fuel

- 509 6. Ketones and levulinates had slightly lower thermal engine efficiency than the 510 reference diesel fuel.
- 511 7. NO_x emissions appeared to be affected by both the in-cylinder temperatures than the
 512 adiabatic flame temperatures of the tested molecules.
- 8. NO_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_x emissions of the oxygenated molecule groups.
- 5169. The oxygenated molecules produced less of the heavy particulates but more of the517light, smaller particulates compared to both alkanes and reference diesel fuel.
- 518 10. No real difference in the mass or the number of particulate emissions was observed519 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.

524 As to be expected, the oxygen bearing molecules show a clear reduction in particulate mass, 525 when compared with the non-oxygen bearing molecules and the fossil diesel fuel used as the 526 reference test fuel. There is however, in the case of the oxygen bearing molecules a penalty in 527 terms of an increase in the number of particulates (compared to reference diesel fuel and non-528 oxygenated molecules) which is particularly relevant due to recently introduced legislation to 529 additional control the number of emitted particles for vehicle engines. The customary penalty of 530 oxygen bearing molecules in terms of some increase in NO_x can also be seen in the results 531 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 nonoxygen 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.

539 APPENDIX I

	Doiling	Density	Surface	Dynamic	Lower	C/H	0	
Fuel molecule	Boiing	at 298 K	tension	Viscosity at	heating	Atomic	(m %)	
	ροπτ	[23]	at 298 K	298 K	value	ratio		
	(K)	(g/ml)	(N/m)	(Pa*s)	(MJ/kg)			
Alkane								
Heptane	372	0.682	0.0198	0.00039	45	0.448	0	
Nonane	424	0.715	0.0224	0.00067	45	0.450	0	
Decane	447	0.73	0.0234	0.00086	44	0.455	0	
Ether								
Dipentyl ether	460	0.785	0.0243	0.00161	39	0.455	10.1	
Ketone								
3-Heptanone	421	0.818	0.0261	0.00075	36	0.5	14.0	
5-Nonanone	462.6	0.826	0 0265	Not	38	05	11 3	
5 Nonanone	[24]	[25]	0.0203	available	50	0.5	11.5	
Levulinate								
Ethyl levulinate	480	1.016	0.0307	Not	24	0.58	33.3	
,				available		0.00	0010	
Butyl levulinate	514	0.974	0.0312	Not	28	0.56	27.9	
,				available				
Valerate				0 000 47				
Ethyl valerate	420	0.875	0.0267	0.00847	31	0.5	24.6	
				[26]				
Butyl valerate	462	0.868	0.0279	NOT	33	0.5	20.3	
Pentyl valerate	481	0.865	0.0283	available	34	0.5	18.6	

540 Physical properties of the tested fuel molecules [23]

542 APPENDIX II

541

543 Results of the combustion experiments

			Maximum			
Fuel molecule	Ignition	Premixed	average	Peak	Timing of	Engine
	delay	phase	in-cylinder	HKK	Peak HRR	efficiency
	(CAD)	(%)	(K)	(J/CAD)	(CAD)	(%)
Alkane	(0)	(* -)	()	(0) 00 00 1	(0.12)	(* - 7
Heptane	5.3	25.7	1481	65.0	359.4	49.4
Nonane	5.1	23.0	1450	60.5	359.5	41.4
Decane	4.7	21.2	1453	52.4	358.8	40.9
Ether						
Dipentyl ether	4.5	45.8	1476	46.0	361.6	44.5
Ketone						
3-Heptanone	6.9	40.8	1506	167.6	363.7	28.5
5-Nonanone	5.9	48.9	1467	131.0	361.1	41.3
Levulinate						
Ethyl levulinate	8.0	80.8	1548	132.4	367.5	44.3
Butyl levulinate	7.4	51.3	1516	177.4	364.7	33.7
Valerate						
Ethyl valerate	7.8	63.0	1529	168.0	365.6	44.0
Butyl valerate	7.2	70.4	1502	165.6	363.3	47.9
Pentyl valerate	6.6	62.5	1496	152.2	362.2	49.1
Reference Diesel	5.7	51.6	1501	132.2	361.1	45.6

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