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Blending lignin-derived oxygenate in enhanced multi-component diesel fuel for improved emissions

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Abstract

Experiments were conducted on a single-cylinder diesel engine to ascertain prospective improvements in engine performance and exhaust emissions with various blends of additised and non-additised diesel fuels. Two fuel additives, cyclic peroxide (3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-hexaoxacyclononane) and cyclohexanol are blended in diesel and or synthetic diesel and there effects on fuel properties, combustion characteristics and emissions were studied. The cyclic peroxide was chosen to be studied for its potential to increase cetane number and reduce engine out emissions when used in multicomponent blends. Its capability as a cetane-enhancer was proven when used at various concentrations in multiple diesel-like fuel blends.

The effects of cyclohexanol, which could be produced from lignocellulosic biomass, are researched when used with additised diesel and a gas to liquid (GTL)-diesel blend. It improved particulate matter (PM) but was particularly effective in combination with a GTL-diesel blend. Its ability to suppress soot formation combined with GTL's non-existent aromatic content caused engine out soot to be reduced by up to 72% but, critically, it also showed a reduction in NO_x in comparison to conventional diesel fuel. This blend has shown significant potential as a fuel as well as its properties fall within EN590's specifications for a diesel fuel.

Keywords: *Lignin, Cyclohexanol, GTL, NO_x, Particulate Matter*

1. Introduction

The diesel engine is highly lauded due to its preferential fuel economy and its reduced CO_2 emissions. Unfortunately, the diesel engine's soot and NO_x emissions which are difficult to be controlled simultaneously, have adverse effects on public health and the environment [1]. Legislations are constantly being brought into the diesel industry to reduce these harmful emissions as well as to continually improve fuel economy. An approach to fulfil the need for enhanced performance and reduced harmful emissions is attainable through the use of new hydrocarbon components and fuel additives in multicomponent fuel blends.

34   The cetane-enhancing additives are mainly used to improve engine performance [2]-[4]. Rode et
35 al. [5]-[6] researched the use of organic peroxides which are chemically similar to the well-known
36 cetane-enhancer di-tertiary butyl peroxide (DTBP) [7]. Where DTBP contains a single peroxide bond
37 Rode et al. looked at peroxides which contained double and treble peroxide bonds – tetraoxanes
38 (dimers) and hexaoxonanes (trimers), respectively. Other authors [8]-[10] also researched the
39 enhancement of the ignition properties of a fuel blend through the addition of cyclic peroxides
40 concluding that peroxide bonds have a predominant role in heat generation through rapid and
41 exothermic oxidative degradation as well as producing enhanced radical chain-reactions during the
42 pre-ignition stage. Furthermore, any cyclic peroxide that lacked the presence of an aromatic ring
43 showed beneficial results at various concentrations while a cyclic hexaoxonane was shown to have the
44 greatest impact by increasing the cetane number by approximately 10 [5]. Therefore, a suitable
45 chemical which has the critical properties of the researched cyclic hexaoxonanes was found and
46 obtained: 3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-hexaoxacyclononane (Figure 1a).

47   Alternatively to cetane-enhancers, oxygenates are used for numerous reasons. The presence of
48 oxygen in the combustion process has a critical impact on soot and, hence, particulate matter (PM)
49 emissions [11]-[12]. This also extends to oxidising the soot itself once formed [13] and as a result
50 improve the exhaust emissions while seamlessly mixing with the diesel fuel [12],[14]-[21]. The main
51 factor in the performance of oxygenates is not only their oxygen content but also the structure of the
52 oxygenate functional group has a significant role. The most effective oxygenates have been seen when
53 an oxygen atom is bonded to multiple carbons [22]. For example, ethers have shown better soot
54 suppression-oxidation efficacy than alcohols which, in turn, are better than esters. Figure 1b shows
55 how the ratio of oxygen-carbon bonds to oxygen atoms decreases from ethers to esters. Research has
56 shown that the presence of an aliphatic (saturated) cyclic ring, in this case through the use of
57 cyclohexanone, has a dramatic effect on soot abatement compared to ordinary oxygenates [23]-[25].
58 The low reactive cyclic oxygenate performed exceptionally well when compared to the more reactive
59 linear and branched oxygenates; though no chemical reasoning as to the cause of such effects is
60 explained. Cyclohexanone's capabilities of reducing smoke emissions are reasoned to be as a result of
61 improved suppression rather than enhanced soot oxidation [24]. Cyclohexanone was also tested
62 against another cyclic oxygenate, cyclohexanol (Figure 1c), where both showed similar effectiveness
63 [24]. It has to be noted that these cyclic hydrocarbon could be derived from non-edible materials such
64 as lignin which is a renewable source of second generation biofuels or biohydrocarbons components.
65 Wild et al. showed how cyclohexanol can be produced as a major constituent through a two-stage
66 method [26].

67   There are many alternative fuels to diesel which have different but attractive fuel properties.
68 Using the Fischer-Tropsch process, fuels such as gas to liquid (GTL) are viable options where a
69 distinct improvement in cetane number is evident. In addition to the benefit to the combustion process

70   there are other properties (almost non-existent sulphur and aromatic content) which are able to assist

71   in the reduction of exhaust emissions – principally NO_x and PM [27]-[29]. The reduction in aromatics

72   is heavily linked to the decrease in soot due to aromatics being intermediaries of soot production. This

73   is an alternate way to reducing PM compared to oxygenates and shows potential to utilise both

74   towards a common goal.

75   Consequently, the potential of the cetane-enhancer (3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-

76   hexaoxacyclononane) and cyclohexanol is assessed in multicomponent blends in terms of engine

77   performance and pollutant emissions.

78   **2. Material and methods**

79   *2.1 Experimental apparatus*

80   Experiments were conducted on a single cylinder direct injection diesel engine which has been

81   used in previous research [30]-[31]. The combustion chamber is a bowl-in-piston design and the test

82   rig consists of a thyristor-controlled DC motor-generator machine dynamometer coupled to a load cell

83   which is used to load and motor the engine. All tests were steady state and set at an engine speed of

84   1500 rpm and indicated mean effective pressure (IMEP) values equal to 3 and 5 bar. To study the

85   effects of exhaust gas recirculation (EGR), the engine was kept running at constant load with EGR

86   ranging from 0 to 20%. The EGR flow was controlled manually by a valve and was determined

87   volumetrically as the percentage reduction in volume flow rate of air.

88   To perform the combustion analysis, LabVIEW based software was used to study the peak

89   cylinder pressure, IMEP and such properties. At each test condition, the cylinder pressure data from

90   200 consecutive engine cycles were acquired and the average value determined. In-cylinder pressure

91   traces were acquired by a Kistler 6125B pressure transducer, with a Kistler 5011 charge amplifier at

92   crank shaft positions, determined by an incremental shaft encoder, with data recorded by data

93   acquisition board National Instruments PCI-MIO-16E-4, installed in a PC. In-house developed

94   LabVIEW based software was used to obtain pressure data and analyse combustion parameters such

95   as the coefficient of variation (COV) of IMEP, peak pressure, indicated power and heat release.

96   A MultiGas 2030 FTIR spectrometry based analyser was used for a range of emissions

97   measurements including NO_x, THC, and CO amongst others. A TSI SMPS 3080 particle number and

98   size classifier with thermodiluter was employed to measure the particle size distribution of PM

99   emitted from the engine. The dilution ratio was 1 part exhaust to 36 parts air. Once the particle

100   number distribution is obtained it can be transformed into volume and later to a particle mass

101   distribution using an agglomerate density function which decreases as agglomerate size increases

102   [30]. Particulate matter was collected on glass micro-fibre filter using a partial flow diluter (dilution

103   ratio 1 part exhaust to 10 parts air) in order to study soot reactivity in an oxidant atmosphere.

104   Particulate matter samples were first pre-treated in an inert atmosphere (pure nitrogen from 40 to

105   600°C with a heating ramp of 3 °C.min^{-1}) to remove the volatile organic material present in the

106   particulate matter. It is believed that after this pre-treatment only carbonaceous material (soot)

107   remains in the filter. Temperature was increased from 150 to 600 °C with a heating ramp of 3 °C.min^{-}

108   ^{1} in an oxidant atmosphere (around 10.5% oxygen in a volumetric basis balance in nitrogen). This

109   oxygen concentration was chosen as it is similar to the exhaust oxygen concentration in the engine

110   operating condition where particulate matter was collected.

111   *2.2 Fuel components and blends*

112   ULSD and GTL were supplied by Shell, while cyclohexanol was provided by LivChem Logistics

113   GmbH and the cetane enhancer by Acros organics. Density, kinematic viscosity and calorific value of

114   fuel component and fuel blends properties were measured in the Future Power System laboratories

115   following the standards ISO 12185, ISO 3105 and ISO 1928, respectively (see Table 1). Every

116   property has been measured three times obtaining an uncertainty around 2% for each property. The

117   molecular formula and cetane numbers of ULSD and GTL were provided by Shell, while the cetane

118   number of cyclohexanol was provided by LivChem Logistics GmbH. It has been assumed that the

119   effect of the cetane enhancer is the same for all the blends and equal to the increase experimentally

120   obtained by [5] when -hexaoxonane derivatives are used. In this work they approximately obtained

121   that an increase of 4 and 10 in the cetane number is obtained when 500 and 1000ppm of the –

122   hexaoxonane derivatives are used. However, the cetane number effect of the rest of blend components

123   ULSD-GTL [27] and cyclohexanol has been considered to be proportional to the volumetric fraction

124   of each component in the blend. In addition other properties such as density and bulk modulus can

125   have on the injector used. A mechanically-injected system is used and relies on the generated pressure

126   to propagate the fuel from the pump to the injector and it is this which is influenced by the fuel

127   properties. By matching the blend properties such as density and cetane number, it is believed that the

128   start of injection and combustion should be similar. As shown in Table 1, the six blends used are:

129   A. ULSD

130   B. ULSD and cyclohexanol (*CH20*)

131   C. ULSD and cetane-enhancer (*CE*)

132   D. ULSD and GTL (*GD30*)

133   E. ULSD, GTL, cyclohexanol and cetane-enhancer (*GD30CH10CE*)

134   F. ULSD, cyclohexanol and cetane-enhancer (*CH10CE)*

135   The majority of blends were produced with fluid properties equivalent to those stated by EN590 –

136   proving their use as a potential fuel (see Table 1). To isolate the effect of cetane number in the

137   comparison between *CE, GD30, GD30CH10CE* and *CH10CE*, the same estimated cetane number is

138   attained. The cetane-enhancer is used in these blends in different concentrations to cancel out

139   cyclohexanol's detrimental effect on the cetane number. *CH10CE* utilises cyclohexanol for its

140   oxygenating ability and also matched the specifications of EN590 – this would have the potential to

4

141 be used commercially, similarly to *ULSD, CE* and *GD30CH10CE*. Furthermore to ascertain the effect

142 of cyclohexanol 20 vol% was used in *CH20* resulting in blend density and cetane number different to

143 the rest of the blends.

3. Results and discussion

3.1 Combustion and Performance

146   By matching the fluid properties, in this case density and cetane number, of *CE, GD30,*

147 *GD30CH10CE* and *CH10CE* the start of injection and combustion of these blends were anticipated to

148 be close to each other. This is confirmed in the combustion patterns at 3 and 5 bar IMEP in Figure 2a

149 and Figure 2b, respectively.

150   The start of combustion (SOC) of these blends occurs at similar crank angle degree (CAD)

151 indicating that the individual properties of each component have been compensated for and that the

152 cetane-enhancer's concentrations match the improvement in CN predicted. It is evident that these

153 fuels also produce comparable in-cylinder pressure and rate of heat release (ROHR). These blends

154 produce the smaller quantity of fuel burnt in premixed combustion due to the reduced combustion

155 delay compared to conventional diesel fuel. On the contrary, *CH20* has the lowest cetane number

156 indicating a retarded combustion where a bigger premixed combustion peak is obtained.

157   The indicated specific fuel consumption (ISFC) (see equation 1) has been calculated using the

158 fuel consumption ($\dot{m}_f$) and indicated power N_i for each fuel. ISFC of the cyclohexanol blend is higher

159 than in the case of conventional diesel fuels and rest of the blends (see Table 2). On the other hand,

160 the indicated specific fuel consumption of the GTL blend is lower than the rest of the blends. The

161 indicated thermal efficiency (ITE, see equation 2) is considered a truer representation of engine

162 performance than ISFC as it accounts for the differences in the lower heating value (LHV) of each

163 blend component. The use of the cetane-enhancer and GTL individually slightly improve the ITE

164 compared to conventional diesel fuel (less than 2%) which it is considered to be within the uncertainty

165 of the measurement. Though it is noticed when both used simultaneously there is little difference

166 between its ITE when compared to *ULSD*'s (see Table 2). Therefore, the difference in the indicated

167 specific fuel consumption of the different blends is attributed to the different heating value of the fuel

168 blends rather than any differences on fuel efficiency, which cannot be considered significant.

$$ISFC\left[\frac{g}{kWh}\right] = \frac{\dot{m}_f}{N_i}$$ **Equation 1:** Indicated specific fuel consumption

$$ITE[\%] = \frac{N_i}{\dot{m}_f \cdot LHV} \cdot 100$$ **Equation 2:** Indicated thermal efficiency

169

3.2 THC and CO emissions

171   Figure 3a shows the THC and CO emissions of each blend when operated at 0% EGR for both

172   engine loads. *CE* shows comparable results to *ULSD* for CO emissions. Therefore, any difference in

173   *CH10CE*'s emissions is due to the use of cyclohexanol. The effect it has been exemplified in *CH20*

174   where twice the vol% is used. As an oxygenate, cyclohexanol would be expected to reduce gaseous

175   carbonaceous emissions. However, with a lower CN, emissions could potentially increase as there is

176   less time for them to oxidise – a result of the retarded combustion. This is in addition to the relatively

177   higher viscosity of the additive. In this case it is apparent that, particularly at 20 vol%, the viscosity

178   and influence of the CN of cyclohexanol takes an effect and results in higher emissions. Table 1 also

179   shows how the C/H ratio for *GD30* is significantly lower than the majority of the other blends. This

180   can explain the lower THC and CO emissions obtained with this fuel blend compared to those with a

181   similar combustion pattern.

3.3 NO_x emissions

183   The differences in NO_x emissions from the combustion of the fuels blends (Figure 3a and Figure

184   3b) are the result of multiple reasons such as cetane number, oxygen content and heat absorption by

185   soot emissions. The high NO_x emissions of *CH20* with respect to the rest of fuel blends could be due

186   to the oxygen content of cyclohexanol and the low cetane number of this blend. A low cetane number

187   produces an increase of ignition delay resulting in a higher premixed/diffusion combustion ratio

188   causing an increase in NO_x emissions [32]. The increase in NO_x emissions due to the presence of

189   cyclohexanol is also seen when compared *CH10CE* with respect to *CE* as well as in the comparison of

190   *CH10CE* to *GD30CH10CE* having similar cetane numbers. Furthermore, it has to be noted that the

191   presence of GTL in *GD30* and *GD30CH10CE* also reduces NO_x emissions, even though the cetane

192   number is comparable to *CH10CE* and *CE*. Therefore GTL compensates for cyclohexanol's

193   disadvantageous effects in *GD30CH10CE* where the blend shows better NO_x performance than for

194   instance *ULSD*. The NO_x emissions trends between fuels are maintained at both engine load used in

195   this study with the exemption of *CE*. The NO_x emissions of *CE* at 3 bar IMEP are higher than those

196   from the combustion of *GD30CH10CE* and *GD30*, even though those differences are close to the

197   significance level of the results (see error bars in Figure 3). However, *CE* shows the lowest NO_x

198   emissions at 5 bar IMEP. This can be explained by the higher particulate matter emissions of *CE* (see

199   next section) which could absorb heat by radiation reducing the flame in-cylinder temperature. When

200   EGR is used at 10 and 20%, the trends shown between the blends is similar with a reduction of

201   approximately 20% seen for every 10% EGR used (see Figure 5).

3.4 PM size distribution

203   As Table 3 shows, the total particle concentration of *ULSD* and *CE* are similar and much higher

204   than the rest of blends. As a result, it is evident that just an increase in cetane number does not

205   significantly improve PM (see Figure 4a and Figure 4b). On the other hand, the use of *CH20* and

206   *GD30* produce almost identical particle size distributions. It seems that the low C/H ratio and absence

207   of aromatic of GTL in GD30 produces similar PM reduction than the oxygen content of cyclohexanol

208   in a 20% blend of cyclohexanol. When both are combined in *GD30CH10CE*, it shows the lowest PM

209   level on the studied blends by combining the cyclohexanol's and GTL ability to suppress soot

210   formation. It shows a significant reduction of 75% in the total number of particles below 100 nm as

211   well as lowering the total particulate mass by approximately 70%. The particulate size distribution of

212   *CH10CE* shows a reduction in the peak PM value similar to *CH20* and *GD30* yet, particularly at 5 bar

213   IMEP (Figure 4b). From the particulate size distributions, it can be concluded that GTL and

214   cyclohexanol not only reduce the total mass and number of the larger particles but also of the smaller

215   ones. At higher EGR values the trends between all the fuels are comparable to those seen here though

216   the particle increase attained from *ULSD* and *GD30* combustion is higher than the other blends.

217   *3.5 PM/NO$_x$ trade-off*

218   The PM/NO$_x$ trade-off is a well-established relationship between two of the most critical

219   emissions in a diesel engine [32]. The magnitude of PM and NO$_x$ produced are much lower when run

220   at 3 bar (Figure 5a) compared to 5 bar (Figure 5b), as would be expected. The individual trends of

221   each blend actually shows how each one reacts to a higher level of EGR and, with that, a decreased

222   level of oxygen and a lower in-cylinder temperature.

223   A crucial comparison to be seen in Figure 5 is the resemblance between the PM/NO$_x$ trade-off of

224   *CH20* to *GD30*. As this shows, the reduction of soot and NO$_x$ emissions is very similar for a 20%

225   blend of cyclohexanol to 30% GTL. Cyclohexanol's emission improvement is significantly seen at the

226   highest EGR level. As EGR increases there is less oxygen available in comparison to the fuel in the

227   combustion chamber. By the addition of an oxygenate component to the fuel blend the local

228   availability of oxygen is greatly increased to these rich fuel pockets and, hence, why a large increase

229   in soot at 20% EGR is not seen unlike ULSD and GD30. In addition to this, it is seen how

230   *GD30CH10CE* utilises both cyclohexanol and GTL beneficial properties to reduce both emissions

231   across all EGR levels which shows both fuel components are able to work together and produce better

232   results than either on their own.

233   *3.6 Soot Oxidation*

234   Utilising the thermogravimetric method outlined in section 2.1, it is evident an increase in

235   temperature causes a loss in weight from soot which indicates it is progressively being oxidised

236   (Figure 6). The accumulative soot oxidation of each blend is shown in Figure 6b. The temperature at

237   which 2% (defined as the start of soot oxidation), 50% (the median soot oxidation temperature) and

238   90% (defined as the end of soot oxidation) of the soot is oxidised can then be calculated from this plot

239   for each blend (see Table 4).

Figure 6 also shows how the presence of oxygen in the parent fuel has a positive influence on oxidising soot. Critically, the beneficial effect of oxygenated fuels on soot oxidation, which has been previously reported for esters [33], ethers [30] and alcohols [31], is shown for the first time with cyclic oxygenates through this work. The presence of the cyclic oxygenate clearly reduces the 2% soot oxidation temperature value (see Figure 6c). This is seen in the soot from the combustion of *CH10CE* and *GD30CH10CE* blends over *ULSD* and *GD30*, respectively. However, Figure 6d it is seen that this effect diminishes at higher soot oxidation levels when in the presence of soot from the combustion of GTL; while *CH10CE* still shows a decreased soot oxidation temperature compared to *ULSD* at 50% soot oxidation, while *GD30* and *GD30CH10CE* now have very similar temperatures. It is also noted that the use of a cetane enhancer shows a slight detrimental effect on the soot oxidation temperature across the entire temperature range.

The derivative of soot oxidation can be calculated for all the fuel blends (Figure 6a). The peak of each blend represents the temperature where maximum oxidation occurs. As this shows, the presence of oxygen, again, has a positive influence while soot from GTL combustion also shows beneficial soot oxidation characteristics. An oxygenated fuel causes the presence of oxygen throughout the primary soot particles which lead to its overall benefit on soot oxidisation. GTL's benefits can be reasoned to its inherent reduction in soot formation causing both smaller primary soot particles and smaller aggregates [34] which increases the surface/volume ratio of the aggregate increasing soot reactivity.

$$-\frac{dm}{dt} = k_c m^n p_{O_2}^r = A\, exp\left(\frac{-E_a}{RT}\right) m^n p_{O_2}^r \qquad \textbf{Equation 3:} \text{ Rate of soot oxidation}$$

$$ln\left(-\frac{dm}{mdt}\right) = ln\left(A p_{O_2}\right) - \frac{-E_a}{R}\frac{1}{T} \qquad \textbf{Equation 4:} \text{ Linear relationship to calculate } E_a$$

The left hand side of Equation 3 represents the derivative plot shown in Figure 6a. In equation 3 m is the actual mass soot, t is the time, k_c is the reaction time constant, p_{O2} is the partial pressure of oxygen, n and r are the reaction order of soot and oxygen respectively, A is the pre-exponential factor, E_a is the activation energy, T is the temperature and R is the universal gas constant. Here, it is assumed that soot oxidation is a first order reaction with respect to actual soot mass and the partial pressure of oxygen. Equation 1 can then be re-arranged to Equation 2 to obtain the activation energy for the soot produced for each blend. The gradient of said straight line is directly related to the activation energy – as seen in Equation 4. It is seen that the lowest activation energies are produced in the presence of oxygenated blends (see Table 4). This is in accordance with the others trends seen in Figure 6.

4. Conclusions

This study has demonstrated significant improvement in exhaust emissions through the design of multicomponent fuels while retaining the combustion patterns of conventional diesel fuel.

272 Furthermore, blend properties are within EN590 specifications and, hence, new engine modification

273 or calibration is not required when these are used.

274   The cetane-enhancer, 3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-hexaoxacyclononane, was seen to

275 correspond to previous research where its use in multiple concentrations achieved the anticipated

276 improvements of CN in each blend; this property was proved by the start of combustion of four

277 diesel-like fuel blends matching each other in their combustion profiles. Cyclohexanol, was able to

278 improve PM emissions significantly across a range of EGR levels, two different loads and when it

279 was used in multiple blends; it also easier the soot oxidation process in corresponding to its lower

280 activation energy. GTL showed exceptional performance in all characteristics of performance and

281 emissions, but when used in a large quantity, it was unable to match EN590's specifications.

282   When both cyclohexanol and GTL are blended the benefits of both fuel components are seen

283 across every emission and performance characteristic. The results indicate that, despite cyclohexanol

284 having a detrimental effect on the CN of the fuel and GTL taking the blends out of EN590

285 specifications, when used together, in this case as a GD30 blend with 10% cyclohexanol, they work

286 harmoniously to improve performance, reduce emissions while countering each-others' deficiencies.

287 There, a highly renewable blend with the excellent oxygenating capabilities of cyclohexanol coupled

288 with GTL's reduced aromatic content is designed which shows great potential as a fuel.

289 **Acknowledgements**

294 **Nomenclature**

295 *A:* pre-exponential factor
296 *CAD*: crank angle degree
297 CE: a blend of ultra-low sulphur diesel and cetane enhancer
298 CH: cyclohexanol
299 CH10CE: a blend of diesel, cyclohexanol and cetane-enhancer
300 CH20: a blend of ultra-low sulphur diesel and cyclohexanol
301 *CN*: cetane number
302 *CO*: carbon monoxide
303 CO_2: carbon dioxide
304 *COV*: coefficient of variation
305 *DTBP*: di-tertiary butyl peroxide
306 E_a: activation energy
307 *EGR*: exhaust gas recirculation
308 *EHN*: 2-ethylhexyl nitrate
309 *EN590*: European diesel fuel standard
310 *FID*: flame ionization detection
311 FTIR: fourier transform infrared
312 *GD30*: a 70:30 diesel and gas to liquid blend

313   GD30CH10CE: a blend of diesel, gas-to-liquid, cyclohexanol and cetane-enhancer

314   *GTL*: gas-to-liquid

315   *IMEP*: indicated mean effective pressure

316   *ISFC*: indicated specific fuel consumption

317   *ITE*: indicated thermal efficiency

318   K_c: reaction time constant

319   LHV: low heating value of the fuel

320   n: reaction order of soot

321   N_i: indicated power

322   *NDIR*: non-dispersive infrared

323   NO_x: nitrous oxides

324   m: actual mass of soot

325    $\dot{m}_f$: fuel consumption

326   O_2: oxygen concentration

327   p: pressure

328   *PAH*: polycyclic aromatic hydrocarbons

329   *PM*: particulate matter

330   r: reaction order of oxygen

331   R: universal gas constant

332   *ROHR*: rate of heat release

333   SMPS: scanning measurement particle spectrometer

334   SOC: start of combustion

335   t: time

336   T: Temperature

337   *THC*: total hydrocarbons

338   *ULSD*: ultra-low sulphur diesel

339

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415

Tables

Table 1: Volume blend ratios, constituent properties and overall blend properties

Blends	ULSD [%]	GTL [%]	Cetane Enhancer		Cyclohexanol [%]
			[ppm]	Estimated Effect [5][6]	
ULSD	100	0	0	-	0
CH20	80	0	0	-	20
CE	100	0	500	7	0
GD30	70	30	0	-	0
GD30CH10CE	63	27	250	4	10
CH10CE	90	0	1000	10	10

Blend Constituents	Density [kg.m^{-3}]	Viscosity [mm^2.s^{-1}]	Cetane Number	Boiling point/T$_{90}$ (°C)	Oxygen [wt%]	LHV [MJ.kg^{-1}]	Aromatic [wt%]	Molecular Formula
ULSD	827	2.47	54	329	0.0	43.0	24.4	$C_{14}H_{26}$
GTL	785	3.50	79	342	0.0	43.9	0.3	$C_{10}H_{21}$
Cetane-enhancer	875	5.00	-	-	36.4	-	0.0	$C_{12}H_{24}O_6$
Cyclohexanol	962	4.60	23	161	16.0	37.2	0.0	$C_6H_{12}O_1$

Blends	Density [kg.m^{-3}]	Viscosity [mm^2.s^{-1}]	Cetane Number	Oxygen [wt%]	Aromatic [wt%]	C/H
ULSD	827	2.47	54	0.00	24.4	6.39
CH20	854	2.89	48	3.61	18.9	6.30
CE	828	2.47	61	0.02	24.4	6.38
GD30	814	2.78	61	0.00	17.6	6.18
GD30CH10CE	829	2.96	61	1.87	15.4	6.16
CH10CE	841	2.68	61	1.85	21.6	6.34

Table 2: Indicated specific fuel consumption and indicated thermal efficiency when run at 0% EGR

Blends	3 bar		5 bar	
	ISFC [g/kWh]	ITE [%]	ISFC [g/kWh]	ITE [%]
ULSD	241.5	34.9	225.9	37.3
CH20	251.2	34.6	236.0	36.8
CE	238.3	35.4	222.4	37.9
GD30	236.7	35.3	220.4	38.0
GD30CH10CE	244.4	34.8	226.7	37.5
CH10CE	247.4	34.6	232.4	36.8

Table 3: Properties of particulate matter at 0% EGR and IMEP values of 3 and 5 bar

Blends	3 bar			5 bar		
	Total Number $[10^6]$	Mean Diameter [nm]	Total Mass $[10^{-9}$ g]	Total Number $[10^6]$	Mean Diameter [nm]	Total Mass $[10^{-9}$ g]
ULSD	10.51	100.08	13.00	16.24	129.28	32.96
CH20	4.96	101.88	6.25	7.63	125.69	14.69
CE	7.79	105.25	9.58	13.82	126.63	27.31
GD30	5.19	97.26	6.22	6.52	130.28	13.66
GD30CH10CE	2.76	104.17	3.70	4.75	140.62	11.47
CH10CE	5.35	112.42	8.03	8.40	153.87	24.04

Table 4: Temperature of soot oxidation and soot activation energy

Blends	Temperature of soot oxidation [°C]			Activation Energy $[kJ.kmol^{-1}]$
	2%	50%	90%	
ULSD	435	505	550	186.5
CE	436	506	550	192.7
GD30	442	502	547	185.7
GD30CH10CE	436	501	548	175.8
CH10CE	428	496	537	173.7

Figure Captions

Figure 1: Chemical structures of (a) 3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-hexaoxacyclononane, (b) an ether, alcohol and ester and (c) cyclohexanol

Figure 2: Combustion profiles of in-cylinder pressure and heat release at 0% EGR and (a) 3 bar IMEP and (b) 5 bar IMEP

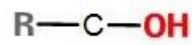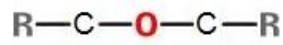**Figure 3:** Gaseous exhaust emissions at 0% EGR and (a) 3 bar IMEP, (b) 5 bar IMEP

Figure 4 Normalised distribution of soot particles at 0% EGR and (a) 3 bar IMEP and (b) 5 bar IMEP

Figure 5: PM/NO$_x$ trade-off at three EGR values and (a) 3 bar IMEP and (b) 5 bar IMEP

Figure 6: (a) Rate of soot oxidation and (b) the accumulative soot oxidation zoomed on (c) 0-5% and (d) 40-60%

(a)

(b)

$R-C-O-C-R$ $R-C-OH$
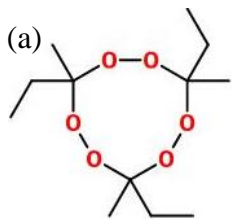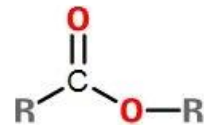
(c)
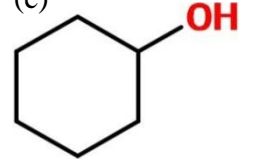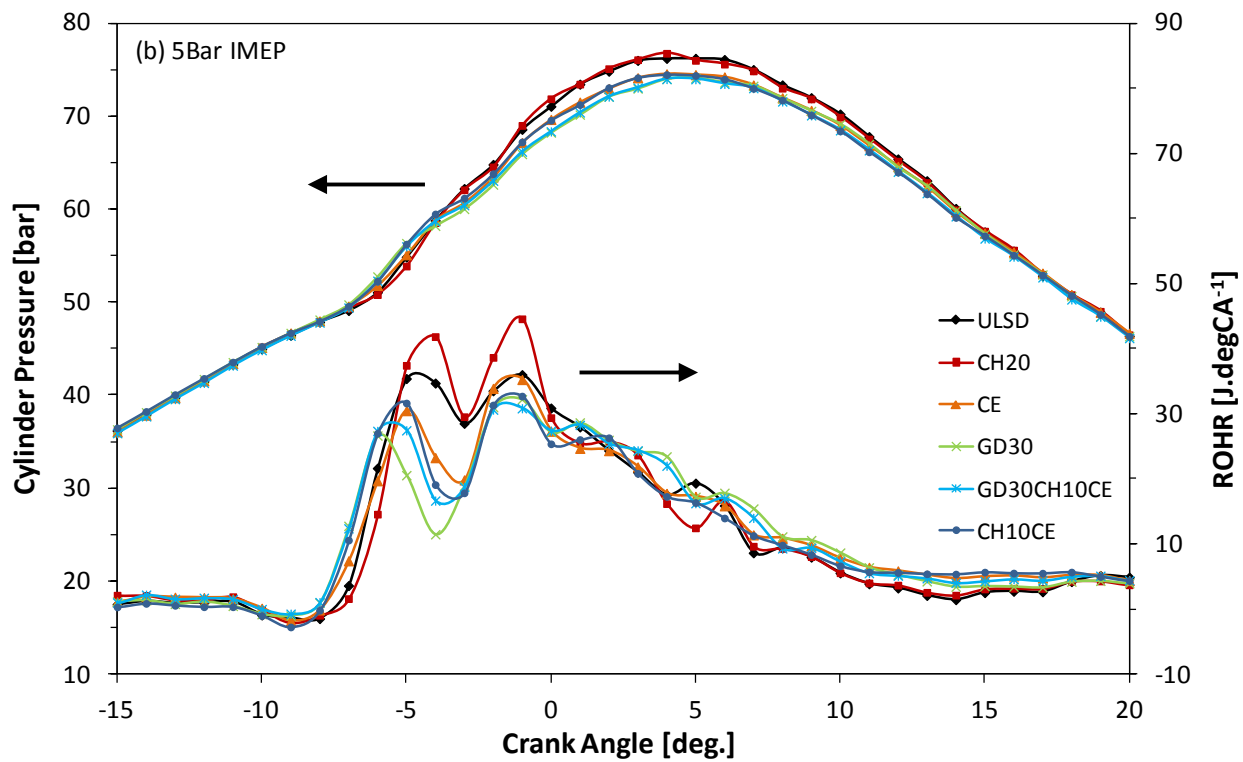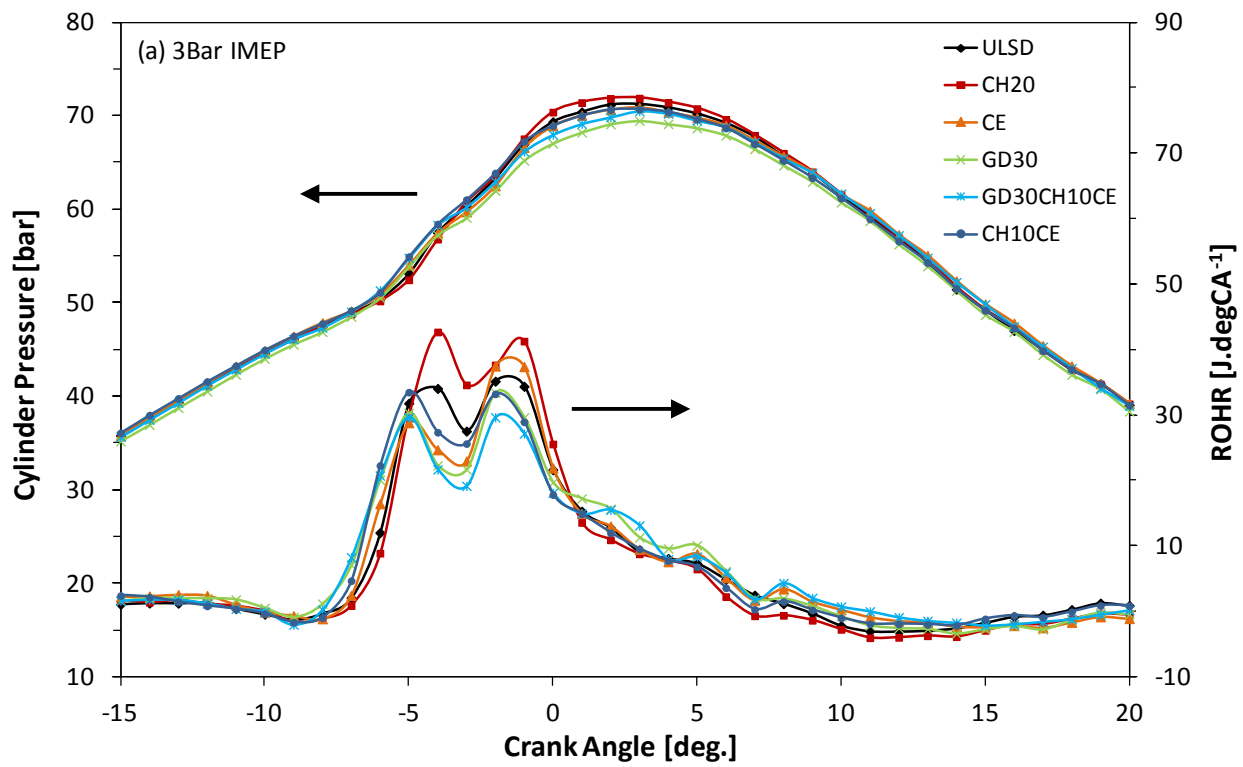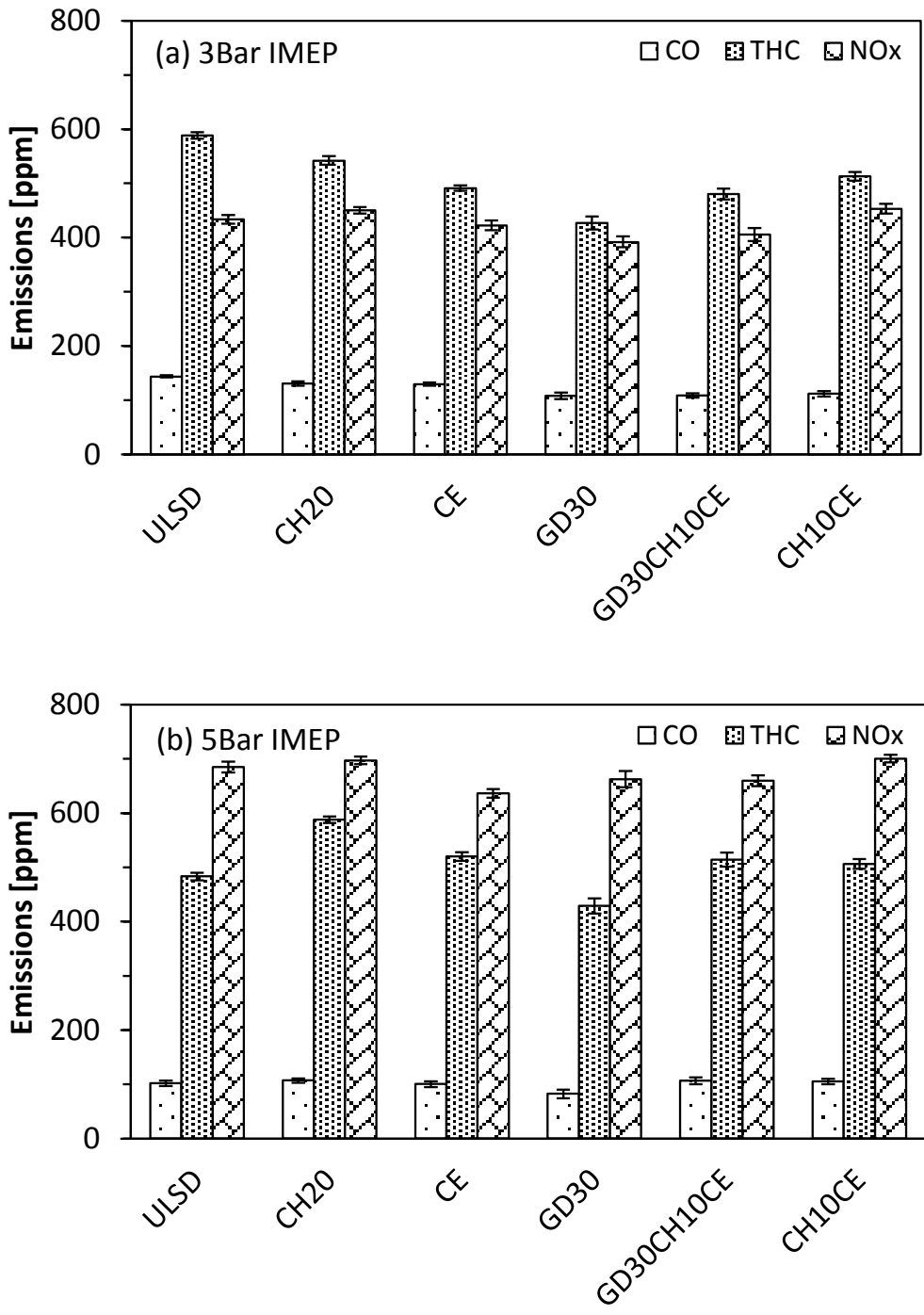
Figure 1

Figure 2

Figure 3
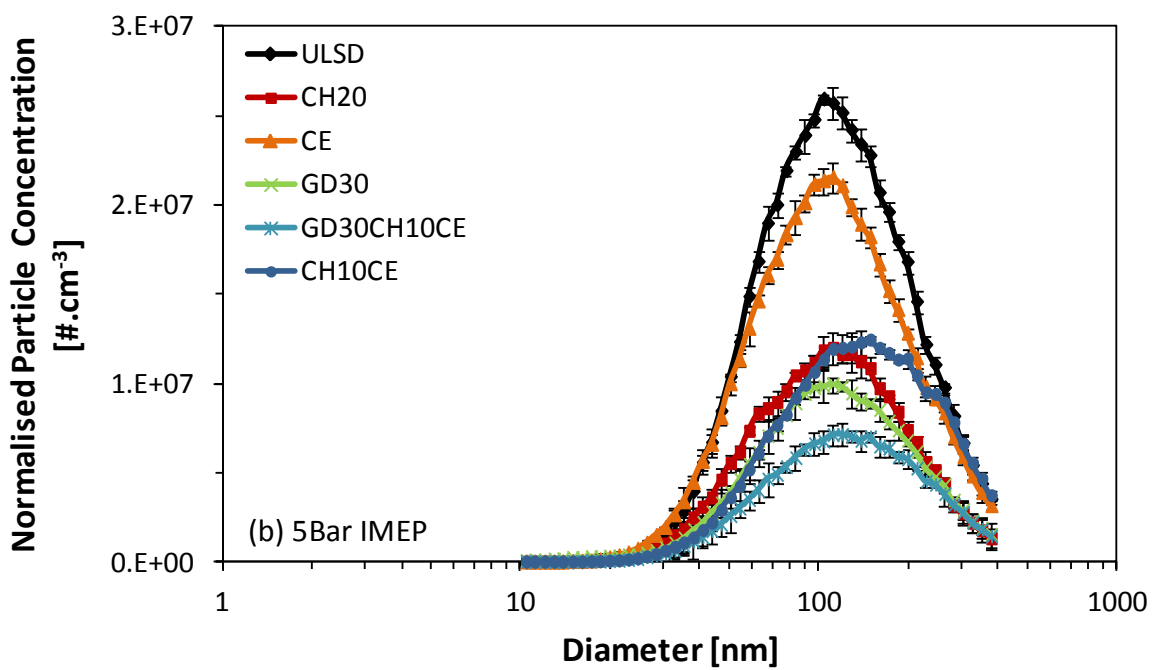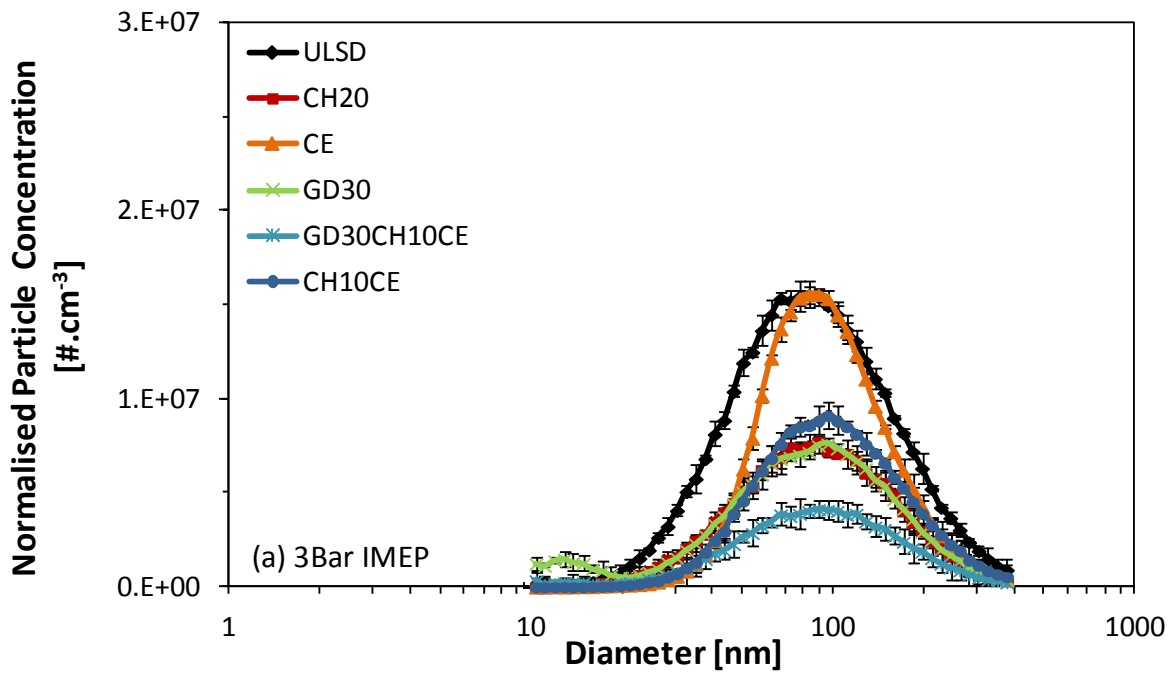
Figure 4

Figure 5

Figure 6