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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⁻¹
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

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.

144 **3. Results and discussion**

145 *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

170 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.

182 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).

202 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).

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

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

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

$$\ln\left(-\frac{dm}{m dt}\right) = \ln(A p_{O_2}^r) - \frac{E_a}{R} \frac{1}{T} \quad \text{Equation 4: Linear relationship to calculate } E_a$$

258 The left hand side of Equation 3 represents the derivative plot shown in Figure 6a. In equation 3
 259 m is the actual mass soot, t is the time, k_c is the reaction time constant, p_{O_2} is the partial pressure of
 260 oxygen, n and r are the reaction order of soot and oxygen respectively, A is the pre-exponential factor,
 261 E_a is the activation energy, T is the temperature and R is the universal gas constant. Here, it is
 262 assumed that soot oxidation is a first order reaction with respect to actual soot mass and the partial
 263 pressure of oxygen. Equation 1 can then be re-arranged to Equation 2 to obtain the activation energy
 264 for the soot produced for each blend. The gradient of said straight line is directly related to the
 265 activation energy – as seen in Equation 4. It is seen that the lowest activation energies are produced in
 266 the presence of oxygenated blends (see Table 4). This is in accordance with the others trends seen in
 267 Figure 6.

268 4. Conclusions

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

271 Furthermore, blend properties are within EN590 specifications and, hence, new engine modification
272 or calibration is not required when these are used.

273 The cetane-enhancer, 3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-hexaoxacyclononane, was seen to
274 correspond to previous research where its use in multiple concentrations achieved the anticipated
275 improvements of CN in each blend; this property was proved by the start of combustion of four
276 diesel-like fuel blends matching each other in their combustion profiles. Cyclohexanol, was able to
277 improve PM emissions significantly across a range of EGR levels, two different loads and when it
278 was used in multiple blends; it also eases the soot oxidation process in corresponding to its lower
279 activation energy. GTL showed exceptional performance in all characteristics of performance and
280 emissions, but when used in a large quantity, it was unable to match EN590's specifications.

281 When both cyclohexanol and GTL are blended the benefits of both fuel components are seen
282 across every emission and performance characteristic. The results indicate that, despite cyclohexanol
283 having a detrimental effect on the CN of the fuel and GTL taking the blends out of EN590
284 specifications, when used together, in this case as a GD30 blend with 10% cyclohexanol, they work
285 harmoniously to improve performance, reduce emissions while countering each-others' deficiencies.
286 There, a highly renewable blend with the excellent oxygenating capabilities of cyclohexanol coupled
287 with GTL's reduced aromatic content is designed which shows great potential as a fuel.

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292 Warwick.

293 **Nomenclature**

294 *A*: pre-exponential factor
295 *CAD*: crank angle degree
296 *CE*: a blend of ultra-low sulphur diesel and cetane enhancer
297 *CH*: cyclohexanol
298 *CH10CE*: a blend of diesel, cyclohexanol and cetane-enhancer
299 *CH20*: a blend of ultra-low sulphur diesel and cyclohexanol
300 *CN*: cetane number
301 *CO*: carbon monoxide
302 *CO₂*: carbon dioxide
303 *COV*: coefficient of variation
304 *DTBP*: di-tertiary butyl peroxide
305 *E_a*: activation energy
306 *EGR*: exhaust gas recirculation
307 *EHN*: 2-ethylhexyl nitrate
308 *EN590*: European diesel fuel standard
309 *FID*: flame ionization detection
310 *FTIR*: fourier transform infrared
311 *GD30*: a 70:30 diesel and gas to liquid blend

312 GD30CH10CE: a blend of diesel, gas-to-liquid, cyclohexanol and cetane-enhancer
313 *GTL*: gas-to-liquid
314 *IMEP*: indicated mean effective pressure
315 *ISFC*: indicated specific fuel consumption
316 *ITE*: indicated thermal efficiency
317 K_c : reaction time constant
318 LHV: low heating value of the fuel
319 n: reaction order of soot
320 N_i : indicated power
321 *NDIR*: non-dispersive infrared
322 NO_x : nitrous oxides
323 m: actual mass of soot
324 \dot{m}_f : fuel consumption
325 O_2 : oxygen concentration
326 p: pressure
327 *PAH*: polycyclic aromatic hydrocarbons
328 *PM*: particulate matter
329 r: reaction order of oxygen
330 R: universal gas constant
331 *ROHR*: rate of heat release
332 SMPS: scanning measurement particle spectrometer
333 SOC: start of combustion
334 t: time
335 T: Temperature
336 *THC*: total hydrocarbons
337 *ULSD*: ultra-low sulphur diesel
338

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414

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/T90 (°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 ₆ H 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	Total Number [10 ⁶]	3 bar		Total Number [10 ⁶]	5 bar	
		Mean Diameter [nm]	Total Mass [10 ⁻⁹ g]		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

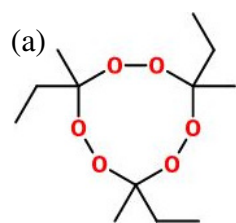
Figure 2: Combustion profiles of in-cylinder pressure and heat release at 0% EGR and (a) 3 bar IMEP and (b) 5 bar IMEP

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

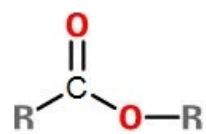
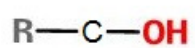
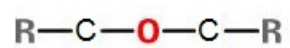
Figure 4 Normalised distribution of soot particles at 0% EGR and (c) 3 bar IMEP and (b) 5 bar IMEP

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%



(b)



(c)

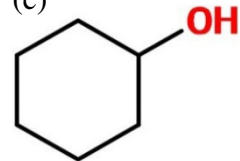


Figure 1

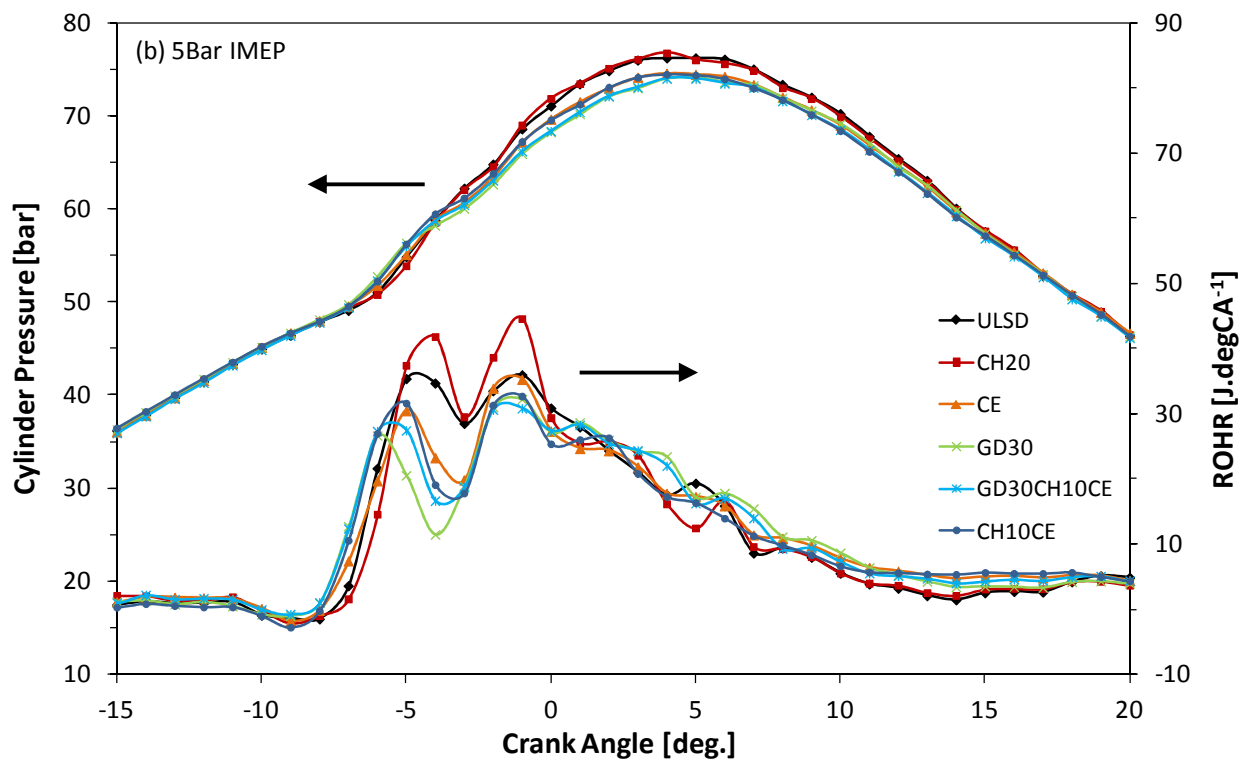
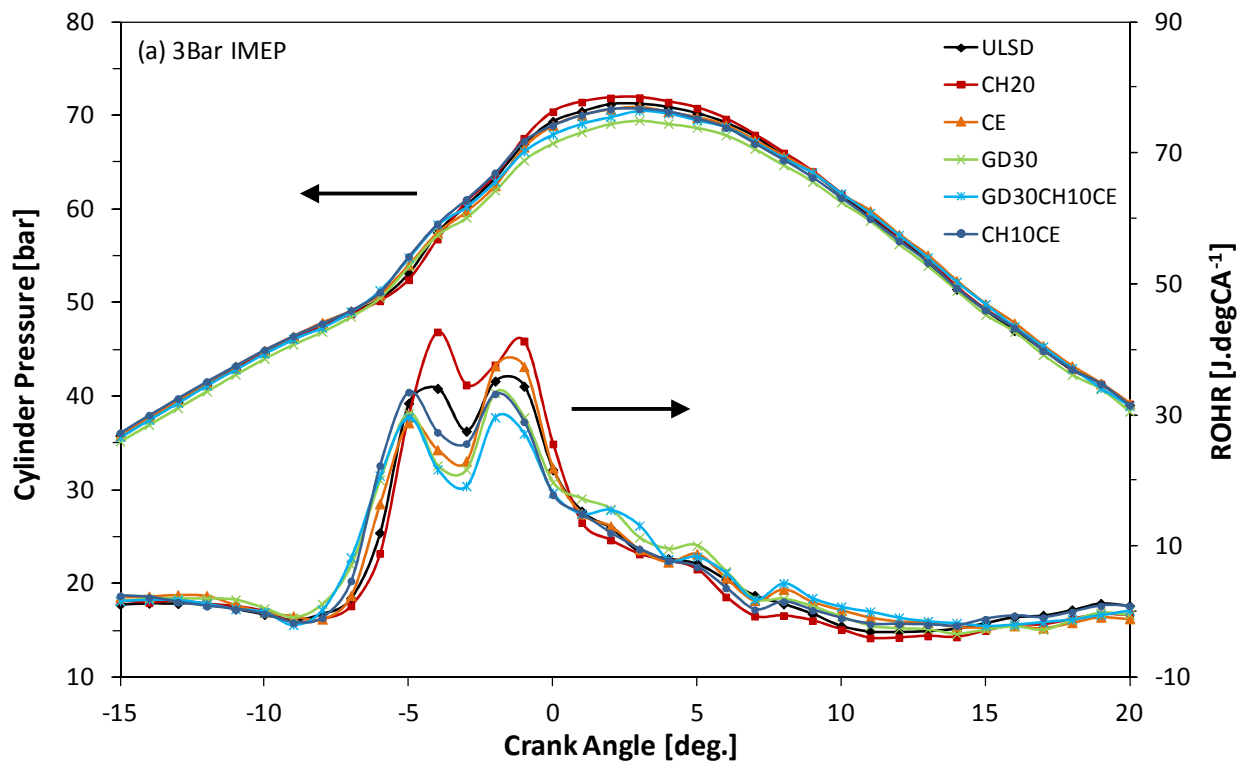


Figure 2

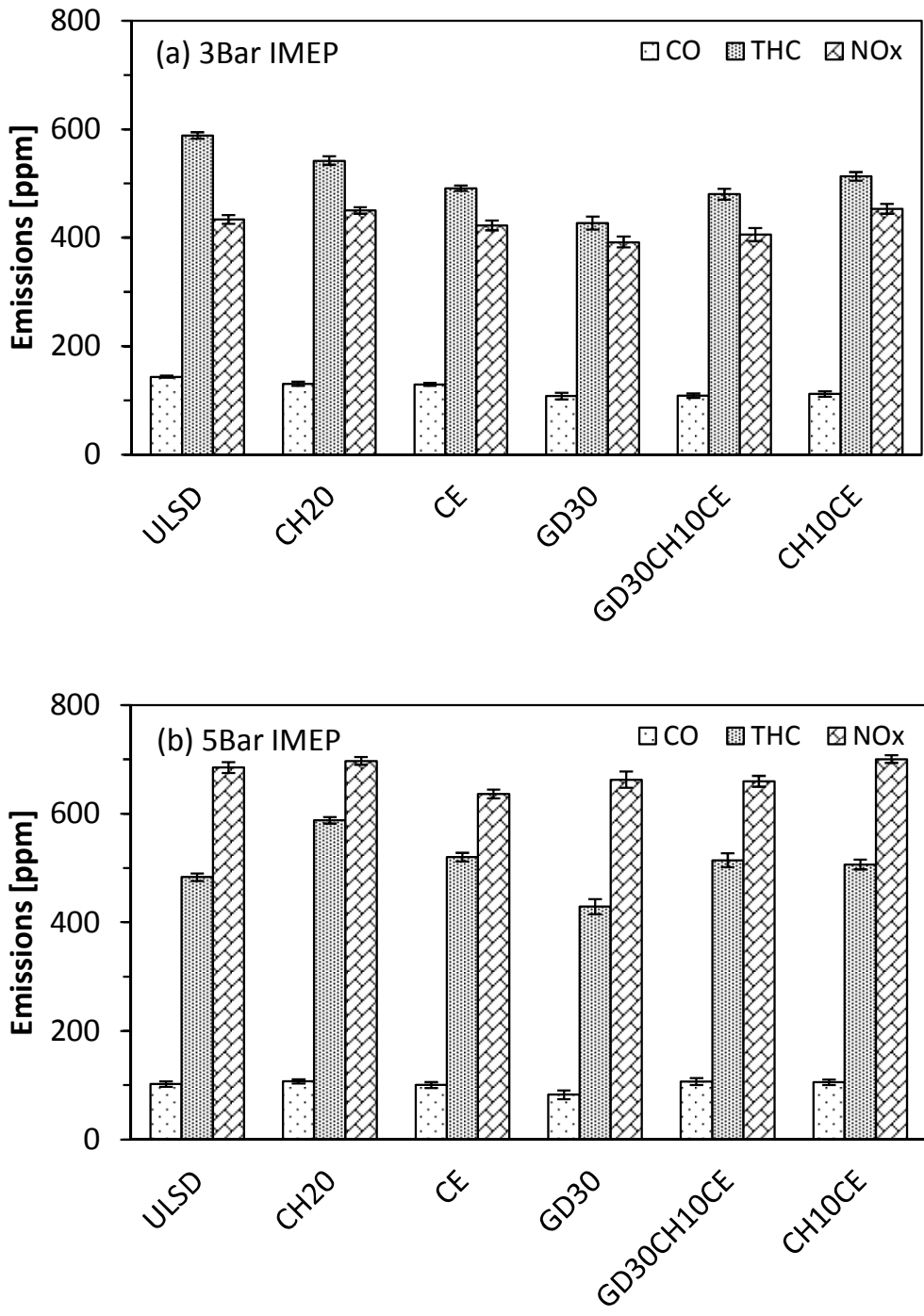


Figure 3

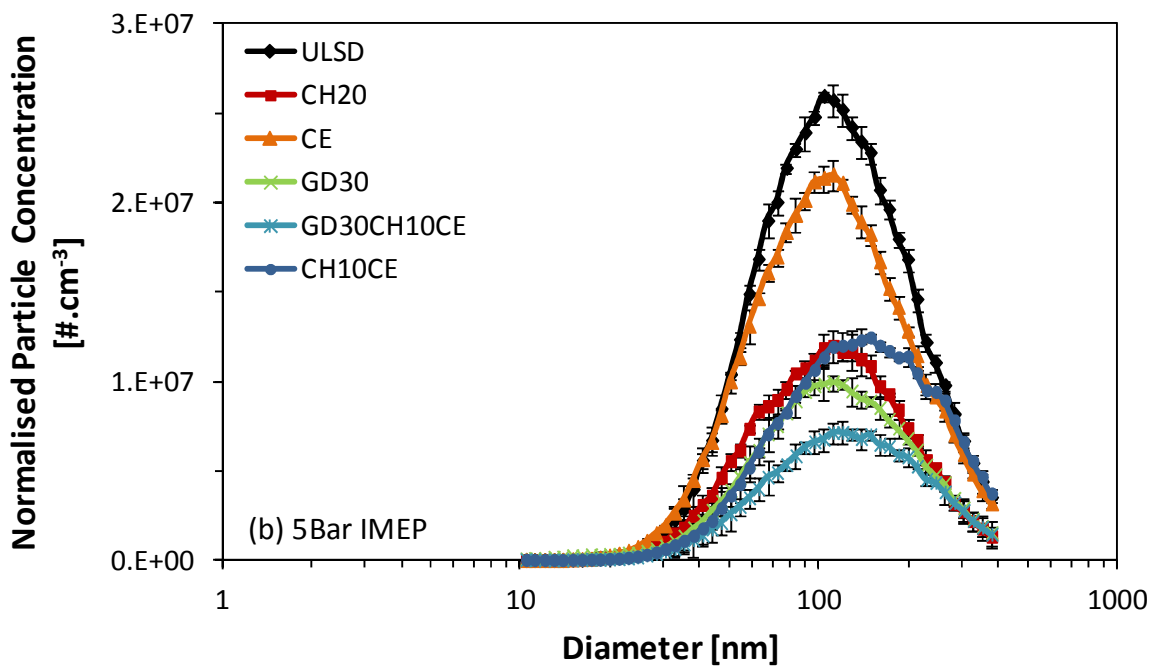
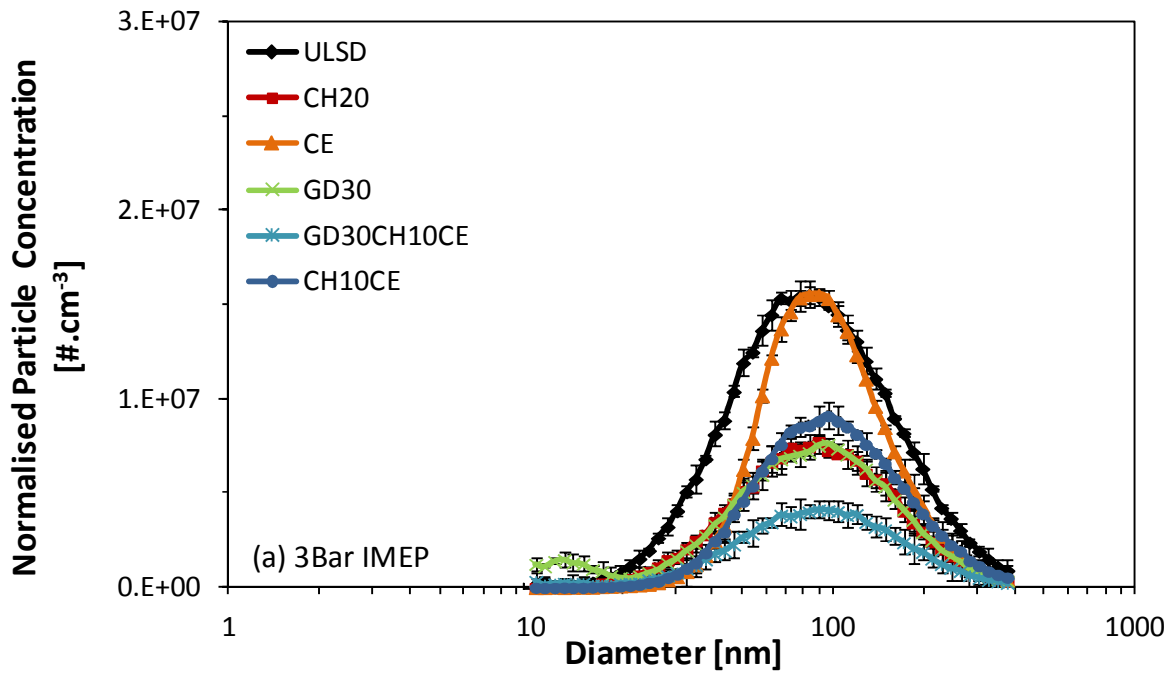


Figure 4

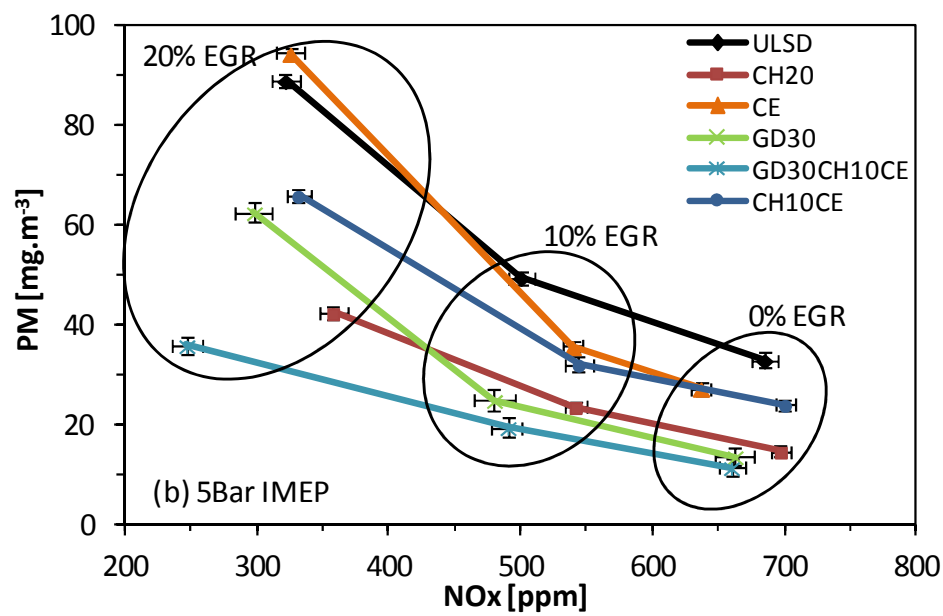
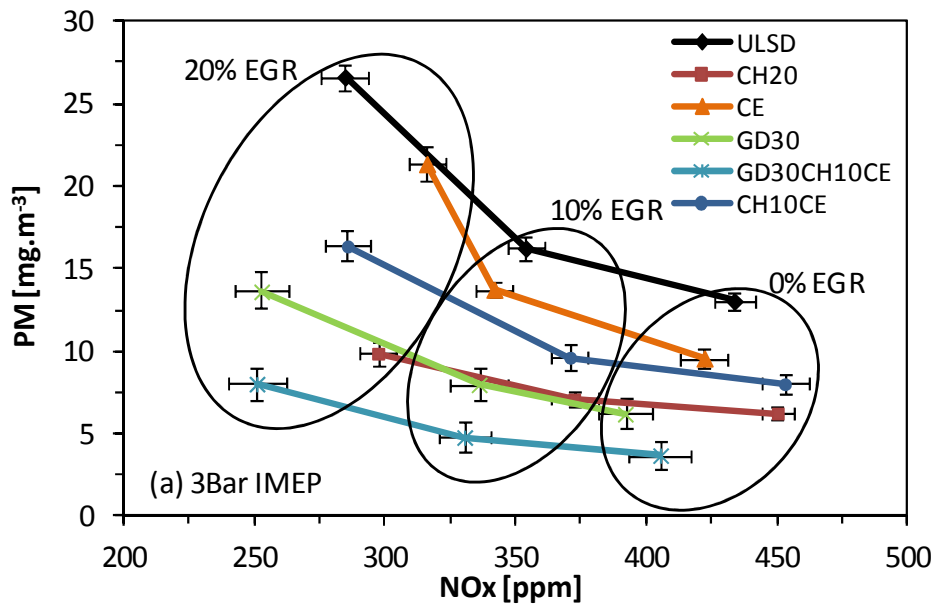


Figure 5

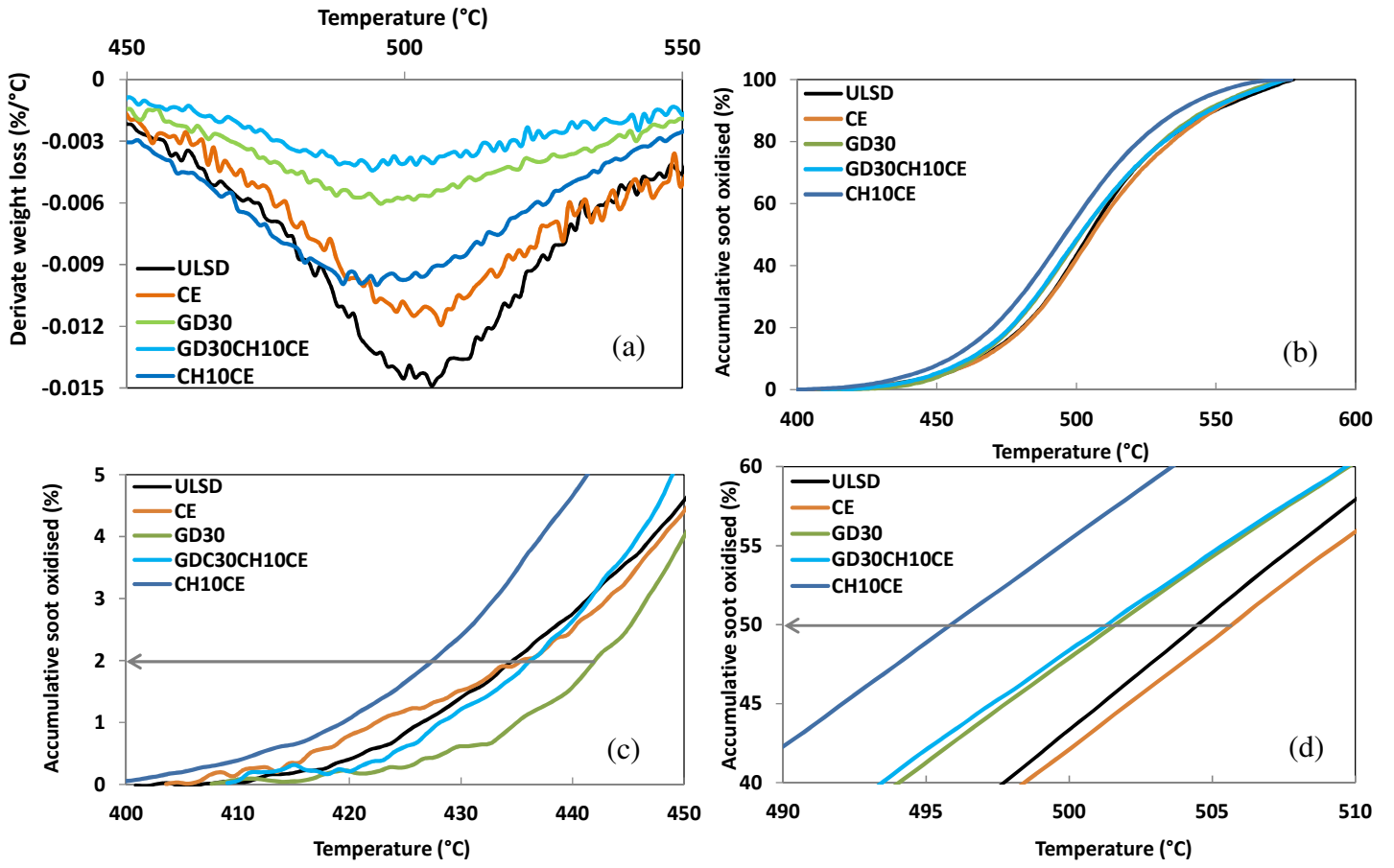


Figure 6