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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.

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

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

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

there are other properties (almost non-existent sulphur and aromatic content) which are able to assist in the reduction of exhaust emissions – principally NO_x and PM [27]-[29]. The reduction in aromatics is heavily linked to the decrease in soot due to aromatics being intermediaries of soot production. This is an alternate way to reducing PM compared to oxygenates and shows potential to utilise both towards a common goal.

Consequently, the potential of the cetane-enhancer (3,6,9-trimethyl-3,6,9-triethyl-1,2,4,5,7,8-hexaoxacyclononane) and cyclohexanol is assessed in multicomponent blends in terms of engine performance and pollutant emissions.

2. Material and methods

2.1 Experimental apparatus

Experiments were conducted on a single cylinder direct injection diesel engine which has been used in previous research [30]-[31]. The combustion chamber is a bowl-in-piston design and the test rig consists of a thyristor-controlled DC motor-generator machine dynamometer coupled to a load cell which is used to load and motor the engine. All tests were steady state and set at an engine speed of 1500 rpm and indicated mean effective pressure (IMEP) values equal to 3 and 5 bar. To study the effects of exhaust gas recirculation (EGR), the engine was kept running at constant load with EGR ranging from 0 to 20%. The EGR flow was controlled manually by a valve and was determined volumetrically as the percentage reduction in volume flow rate of air.

To perform the combustion analysis, LabVIEW based software was used to study the peak cylinder pressure, IMEP and such properties. At each test condition, the cylinder pressure data from 200 consecutive engine cycles were acquired and the average value determined. In-cylinder pressure traces were acquired by a Kistler 6125B pressure transducer, with a Kistler 5011 charge amplifier at crank shaft positions, determined by an incremental shaft encoder, with data recorded by data acquisition board National Instruments PCI-MIO-16E-4, installed in a PC. In-house developed LabVIEW based software was used to obtain pressure data and analyse combustion parameters such as the coefficient of variation (COV) of IMEP, peak pressure, indicated power and heat release.

A MultiGas 2030 FTIR spectrometry based analyser was used for a range of emissions measurements including NO_x, THC, and CO amongst others. A TSI SMPS 3080 particle number and size classifier with thermodiluter was employed to measure the particle size distribution of PM emitted from the engine. The dilution ratio was 1 part exhaust to 36 parts air. Once the particle number distribution is obtained it can be transformed into volume and later to a particle mass distribution using an agglomerate density function which decreases as agglomerate size increases [30]. Particulate matter was collected on glass micro-fibre filter using a partial flow diluter (dilution ratio 1 part exhaust to 10 parts air) in order to study soot reactivity in an oxidant atmosphere. Particulate matter samples were first pre-treated in an inert atmosphere (pure nitrogen from 40 to

600°C with a heating ramp of 3 °C.min⁻¹) to remove the volatile organic material present in the particulate matter. It is believed that after this pre-treatment only carbonaceous material (soot) remains in the filter. Temperature was increased from 150 to 600 °C with a heating ramp of 3 °C.min⁻¹ in an oxidant atmosphere (around 10.5% oxygen in a volumetric basis balance in nitrogen). This oxygen concentration was chosen as it is similar to the exhaust oxygen concentration in the engine operating condition where particulate matter was collected.

2.2 Fuel components and blends

ULSD and GTL were supplied by Shell, while cyclohexanol was provided by LivChem Logistics GmbH and the cetane enhancer by Acros organics. Density, kinematic viscosity and calorific value of fuel component and fuel blends properties were measured in the Future Power System laboratories following the standards ISO 12185, ISO 3105 and ISO 1928, respectively (see Table 1). Every property has been measured three times obtaining an uncertainty around 2% for each property. The molecular formula and cetane numbers of ULSD and GTL were provided by Shell, while the cetane number of cyclohexanol was provided by LivChem Logistics GmbH. It has been assumed that the effect of the cetane enhancer is the same for all the blends and equal to the increase experimentally obtained by [5] when -hexaoxonane derivatives are used. In this work they approximately obtained that an increase of 4 and 10 in the cetane number is obtained when 500 and 1000ppm of the – hexaoxonane derivatives are used. However, the cetane number effect of the rest of blend components ULSD-GTL [27] and cyclohexanol has been considered to be proportional to the volumetric fraction of each component in the blend. In addition other properties such as density and bulk modulus can have on the injector used. A mechanically-injected system is used and relies on the generated pressure to propagate the fuel from the pump to the injector and it is this which is influenced by the fuel properties. By matching the blend properties such as density and cetane number, it is believed that the start of injection and combustion should be similar. As shown in Table 1, the six blends used are:

- A. ULSD
- B. ULSD and cyclohexanol (*CH20*)
- C. ULSD and cetane-enhancer (*CE*)
- D. ULSD and GTL (*GD30*)
- E. ULSD, GTL, cyclohexanol and cetane-enhancer (*GD30CH10CE*)
- F. ULSD, cyclohexanol and cetane-enhancer (*CH10CE*)

The majority of blends were produced with fluid properties equivalent to those stated by EN590 – proving their use as a potential fuel (see Table 1). To isolate the effect of cetane number in the comparison between *CE*, *GD30*, *GD30CH10CE* and *CH10CE*, the same estimated cetane number is attained. The cetane-enhancer is used in these blends in different concentrations to cancel out cyclohexanol's detrimental effect on the cetane number. *CH10CE* utilises cyclohexanol for its oxygenating ability and also matched the specifications of EN590 – this would have the potential to

be used commercially, similarly to *ULSD*, *CE* and *GD30CH10CE*. Furthermore to ascertain the effect of cyclohexanol 20 vol% was used in *CH20* resulting in blend density and cetane number different to the rest of the blends.

3. Results and discussion

3.1 Combustion and Performance

By matching the fluid properties, in this case density and cetane number, of *CE*, *GD30*, *GD30CH10CE* and *CH10CE* the start of injection and combustion of these blends were anticipated to be close to each other. This is confirmed in the combustion patterns at 3 and 5 bar IMEP in Figure 2a and Figure 2b, respectively.

The start of combustion (SOC) of these blends occurs at similar crank angle degree (CAD) indicating that the individual properties of each component have been compensated for and that the cetane-enhancer's concentrations match the improvement in CN predicted. It is evident that these fuels also produce comparable in-cylinder pressure and rate of heat release (ROHR). These blends produce the smaller quantity of fuel burnt in premixed combustion due to the reduced combustion delay compared to conventional diesel fuel. On the contrary, *CH20* has the lowest cetane number indicating a retarded combustion where a bigger premixed combustion peak is obtained.

The indicated specific fuel consumption (ISFC) (see equation 1) has been calculated using the fuel consumption (\dot{m}_f) and indicated power N_i for each fuel. ISFC of the cyclohexanol blend is higher than in the case of conventional diesel fuels and rest of the blends (see Table 2). On the other hand, the indicated specific fuel consumption of the GTL blend is lower than the rest of the blends. The indicated thermal efficiency (ITE, see equation 2) is considered a truer representation of engine performance than ISFC as it accounts for the differences in the lower heating value (LHV) of each blend component. The use of the cetane-enhancer and GTL individually slightly improve the ITE compared to conventional diesel fuel (less than 2%) which it is considered to be within the uncertainty of the measurement. Though it is noticed when both used simultaneously there is little difference between its ITE when compared to *ULSD*'s (see Table 2). Therefore, the difference in the indicated specific fuel consumption of the different blends is attributed to the different heating value of the fuel 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

3.2 THC and CO emissions

Figure 3a shows the THC and CO emissions of each blend when operated at 0% EGR for both engine loads. *CE* shows comparable results to *ULSD* for CO emissions. Therefore, any difference in *CH10CE*'s emissions is due to the use of cyclohexanol. The effect it has been exemplified in *CH20* where twice the vol% is used. As an oxygenate, cyclohexanol would be expected to reduce gaseous carbonaceous emissions. However, with a lower CN, emissions could potentially increase as there is less time for them to oxidise – a result of the retarded combustion. This is in addition to the relatively higher viscosity of the additive. In this case it is apparent that, particularly at 20 vol%, the viscosity and influence of the CN of cyclohexanol takes an effect and results in higher emissions. Table 1 also shows how the C/H ratio for *GD30* is significantly lower than the majority of the other blends. This can explain the lower THC and CO emissions obtained with this fuel blend compared to those with a similar combustion pattern.

3.3 NO_x emissions

The differences in NO_x emissions from the combustion of the fuels blends (Figure 3a and Figure 3b) are the result of multiple reasons such as cetane number, oxygen content and heat absorption by soot emissions. The high NO_x emissions of *CH20* with respect to the rest of fuel blends could be due to the oxygen content of cyclohexanol and the low cetane number of this blend. A low cetane number produces an increase of ignition delay resulting in a higher premixed/diffusion combustion ratio causing an increase in NO_x emissions [32]. The increase in NO_x emissions due to the presence of cyclohexanol is also seen when compared *CH10CE* with respect to *CE* as well as in the comparison of *CH10CE* to *GD30CH10CE* having similar cetane numbers. Furthermore, it has to be noted that the presence of GTL in *GD30* and *GD30CH10CE* also reduces NO_x emissions, even though the cetane number is comparable to *CH10CE* and *CE*. Therefore GTL compensates for cyclohexanol's disadvantageous effects in *GD30CH10CE* where the blend shows better NO_x performance than for instance *ULSD*. The NO_x emissions trends between fuels are maintained at both engine load used in this study with the exemption of *CE*. The NO_x emissions of *CE* at 3 bar IMEP are higher than those from the combustion of *GD30CH10CE* and *GD30*, even though those differences are close to the significance level of the results (see error bars in Figure 3). However, *CE* shows the lowest NO_x emissions at 5 bar IMEP. This can be explained by the higher particulate matter emissions of *CE* (see next section) which could absorb heat by radiation reducing the flame in-cylinder temperature. When EGR is used at 10 and 20%, the trends shown between the blends is similar with a reduction of approximately 20% seen for every 10% EGR used (see Figure 5).

3.4 PM size distribution

As Table 3 shows, the total particle concentration of *ULSD* and *CE* are similar and much higher than the rest of blends. As a result, it is evident that just an increase in cetane number does not significantly improve PM (see Figure 4a and Figure 4b). On the other hand, the use of *CH20* and

GD30 produce almost identical particle size distributions. It seems that the low C/H ratio and absence of aromatic of GTL in *GD30* produces similar PM reduction than the oxygen content of cyclohexanol in a 20% blend of cyclohexanol. When both are combined in *GD30CH10CE*, it shows the lowest PM level on the studied blends by combining the cyclohexanol's and GTL ability to suppress soot formation. It shows a significant reduction of 75% in the total number of particles below 100 nm as well as lowering the total particulate mass by approximately 70%. The particulate size distribution of *CH10CE* shows a reduction in the peak PM value similar to *CH20* and *GD30* yet, particularly at 5 bar IMEP (Figure 4b). From the particulate size distributions, it can be concluded that GTL and cyclohexanol not only reduce the total mass and number of the larger particles but also of the smaller ones. At higher EGR values the trends between all the fuels are comparable to those seen here though the particle increase attained from *ULSD* and *GD30* combustion is higher than the other blends.

3.5 PM/NO_x trade-off

The PM/NO_x trade-off is a well-established relationship between two of the most critical emissions in a diesel engine [32]. The magnitude of PM and NO_x produced are much lower when run at 3 bar (Figure 5a) compared to 5 bar (Figure 5b), as would be expected. The individual trends of each blend actually shows how each one reacts to a higher level of EGR and, with that, a decreased level of oxygen and a lower in-cylinder temperature.

A crucial comparison to be seen in Figure 5 is the resemblance between the PM/NO_x trade-off of *CH20* to *GD30*. As this shows, the reduction of soot and NO_x emissions is very similar for a 20% blend of cyclohexanol to 30% GTL. Cyclohexanol's emission improvement is significantly seen at the highest EGR level. As EGR increases there is less oxygen available in comparison to the fuel in the combustion chamber. By the addition of an oxygenate component to the fuel blend the local availability of oxygen is greatly increased to these rich fuel pockets and, hence, why a large increase in soot at 20% EGR is not seen unlike *ULSD* and *GD30*. In addition to this, it is seen how *GD30CH10CE* utilises both cyclohexanol and GTL beneficial properties to reduce both emissions across all EGR levels which shows both fuel components are able to work together and produce better results than either on their own.

3.6 Soot Oxidation

Utilising the thermogravimetric method outlined in section 2.1, it is evident an increase in temperature causes a loss in weight from soot which indicates it is progressively being oxidised (Figure 6). The accumulative soot oxidation of each blend is shown in Figure 6b. The temperature at which 2% (defined as the start of soot oxidation), 50% (the median soot oxidation temperature) and 90% (defined as the end of soot oxidation) of the soot is oxidised can then be calculated from this plot 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.

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

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

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_{O_2} 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.

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

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

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

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Nomenclature

A: pre-exponential factor
CAD: crank angle degree
CE: a blend of ultra-low sulphur diesel and cetane enhancer
CH: cyclohexanol
CH10CE: a blend of diesel, cyclohexanol and cetane-enhancer
CH20: a blend of ultra-low sulphur diesel and cyclohexanol
CN: cetane number
CO: carbon monoxide
CO₂: carbon dioxide
COV: coefficient of variation
DTBP: di-tertiary butyl peroxide
E_a: activation energy
EGR: exhaust gas recirculation
EHN: 2-ethylhexyl nitrate
EN590: European diesel fuel standard
FID: flame ionization detection
FTIR: fourier transform infrared
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

340 References

- 341 [1] Lin CY, Pan JY. The effects of sodium sulfate on the emissions characteristics of an emulsified marine
342 diesel oil-fired furnace. *Ocean Eng.* 2001;28(4):347–60.
- 343 [2] Ahmed ST, Chaichan MT. Effect of fuel cetane number on multi-cylinders direct injection diesel engine
344 performance and exhaust emissions. *Al-Khwar. Eng. J.* 2012;8(1):65-75.
- 345 [3] Ickes AM, Bohac SV, Assanis DN. Effect of Fuel Cetane Number on a Premixed Diesel Combustion
346 Mode. *Int. J. Engine Res.* 2009;10:251-63.
- 347 [4] Suppes GJ, Goff M, Burkhart ML, Bockwinkel K, Mason MH, Botts JB et al. Multifunctional Diesel Fuel
348 Additives from Triglycerides. *Energ Fuel.* 2001;15:151-7.
- 349 [5] Rode AB, Chung K, Kim YW, Hong IS. Synthesis and cetane-improving performance of 1,2,4,5-
350 tetraoxane and 1,2,4,5,7,8-hexaoxonane derivatives. *Energ Fuel.* 2010;24:1636-9.
- 351 [6] Rode AB, Thajudeen H, Chung K, Kim YW, Hong IS. Synthesis and evaluation of stearic acid derivatives
352 as cetane number improvers. *Bull. Korean Chem. Soc.* 2011;32(6):1965-9.
- 353 [7] Bacha J, Freel J, Gibbs A, Gibbs L, Hemighaus G, Hoekam K et al. Diesel Fuels Technical Review,
354 Chevron. MS-9915 (06-07) 2007.
- 355 [8] Al-Rubaie MAR, Griffiths JF, Sheppard CGW. Some observation on the effectiveness of additives for
356 reducing the ignition delay period of diesel fuels. *SAE Paper* 1991;912333.
- 357 [9] Hashimoto K, Ikeda M, Arai M, Tamura M. Cetane number improvement of diesel fuel by autoxidation.
358 *Energ Fuel.* 1996;10:1147–9.
- 359 [10] Opsenica I, Terzic N, Opsenica D, Angelovsk, D, Lehnig M, Eilbracht P et al. Tetraoxane antimalarials
360 and their reaction with FE(II). *Med. Chem.* 2006;49(13):3790–9.
- 361 [11] Miyamoto N, Ogawa H, Nurn NA, Obata K, Arima T. Smokeless, low NOx, high thermal efficiency, and
362 low noise diesel combustion with oxygenated agents as main fuel. *SAE Paper* 1998;980506.
- 363 [12] Lin CY, Huang JC. An oxygenating additive for improving the performance and emission characteristics
364 of marine diesel engines. *Ocean Eng.* 2003;30:1699-715.
- 365 [13] Tsurutani K, Takei Y, Fujimoto Y, Matsudaira J, Kumamoto M. The effects of fuel properties and
366 oxygenates on diesel exhaust emissions. *SAE Paper* 1995;952349.
- 367 [14] Zhou L, Boot MD, Luijten CCM, Leermakers CAJ, Dam NJ, de Goey LPH. Emission performance of
368 lignin-derived cyclic oxygenates in a heavy-duty diesel engine. *SAE Paper* 2012-01-1056.
- 369 [15] McCormick RL, Ross JD, Graboski MS. Effect of Several Oxygenates on Regulated Emissions from
370 Heavy-Duty Diesel Engines. *Environ. Sci. Technol.* 1997;31:1144–50.
- 371 [16] Rahmat N, Abdullah AZ, Mohamed AR. Recent progress on innovative and potential technologies for
372 glycerol transformation into fuel additives: A critical review. *Renew Sust Energ Rev.* 2010;14:987-1000.
- 373 [17] Yanfeng G, Shenghua L, Hejun G, Tiegang H, Longbao Z. A new diesel oxygenate additive and its effects
374 on engine combustion and emissions. *Appl. Therm. Eng.* 2007;27:202-7.
- 375 [18] Hulwan DB, Joshi SV. Performance, emission and combustion characteristic of a multicylinder DI diesel
376 engine running on diesel–ethanol–biodiesel blends of high ethanol content. *Appl. Energy* 2001;88:5042–
377 55.
- 378 [19] Campos-Fernandez J, Arnal JM, Gomez J, Dorado MP. A comparison of performance of higher
379 alcohols/diesel fuel blends in a diesel engine. *Appl. Energy* 2012;95:267-75.
- 380 [20] Muralidharan K, Vasudevan D. Performance, emission and combustion characteristics of a variable
381 compression ratio engine using methyl esters of waste cooking oil and diesel blends. *Appl. Energy*
382 2011;88(11):3959-68.
- 383 [21] An H, Yang WM, Chou SK, Chua KJ. Combustion and emissions characteristics of diesel engine fuelled
384 by biodiesel at partial load conditions. *Appl. Energy* 2012;99:363-71.
- 385 [22] Boot MD, Frijters PJM, Klein-Douwel RJH, Baert RSG. Oxygenated fuel composition impact on heavy-
386 duty diesel engine emissions. *SAE Paper* 2007-01-2018.
- 387 [23] Boot M, Frijters P, Luijten C, Somers B, Baert R, Donkerbroek A et al. Cyclic Oxygenates: A New Class
388 of Second-Generation Biofuels for Diesel Engines? *Energ Fuel.* 2009;23:1808-17.
- 389 [24] Klein-Douwel RJH, Donkerbroek AJ, van Vliet, Boot MD, Somers LMT, Baert RSG et al. Soot and
390 chemiluminescence in diesel combustion of bio-derived, oxygenated and reference fuels. *Proc. Combust.*
391 *Inst.* 2009;32:2817-25.
- 392 [25] Zhou L, Leermakers CAJ, Luijten CCM, van den Berge B, de Goey LPH. Soot emission of a CI engine
393 fuelled with various PRF/oxygenate blends. *Proceedings of the 5th European Combustion Meeting* 2011.
- 394 [26] De Wild P, Van der Laan R, Kloekhorst A, Heeres HJ. Lignin valorisation for chemicals and
395 (transportation) fuels via (catalytic) pyrolysis and Hydrodeoxygenation. *Environ. Prog. Sustainable*
396 *Energy.* 2009;28(3):461-9.
- 397 [27] Gill SS, Tsolakis A, Dearn KD, Rodriguez-Fernandez J. Combustion characteristics and emissions of
398 Fischer-Tropsch diesel fuels in IC engine. *Prog. Energy Combust. Sci.* 2011;37:503-23.

- [28] Mancaruso E, Vaglieco BM. Premixed combustion of GTL and RME fuels in a single cylinder research engine. *Appl. Energy* 2012;91(1):385-94.
- [29] Armas O, Garcia-Contreras R, Ramos A. Impact of alternative fuels on performance and pollutant emissions of a light duty engine tested under the new European driving cycle. *Appl. Energy* 2013;107:183-90.
- [30] Gill SS, Tsolakis A, Herreros JM, York APE. Diesel emissions improvements through the use of biodiesel or oxygenated blending components. *Fuel* 2012;95:578-86.
- [31] Sukjit E, Herreros JM, Piaszyk J, Dearn KD, Tsolakis A. Finding synergies in fuels properties for the design of renewable fuels – Hydroxylated biodiesel effects on butanol-diesel blends. *Environ. Sci. Technol.* 2013;47:3535-42.
- [32] Armas O, Garcia-Contreras R, Ramos A. Pollutant emissions from engine starting with ethanol and butanol diesel blends. *Fuel Process. Technol.* 2012;100:63–72.
- [33] Song J, Alam M, Boehman AL, Kim U. Examination of the oxidation behaviour of biodiesel soot. *Combust. Flame* 2006;146(4):589-604.
- [34] Herreros JM. PhD thesis. Fuel effects in size, morphology and microstructure of diesel particulate matter. 2009. University of Castilla-La Mancha (Spain).

Tables

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

Blends	ULSD [%]	GTL [%]	Cetane Enhancer [ppm]	Estimated Effect [5][6]	Cyclohexanol [%]
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 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	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%



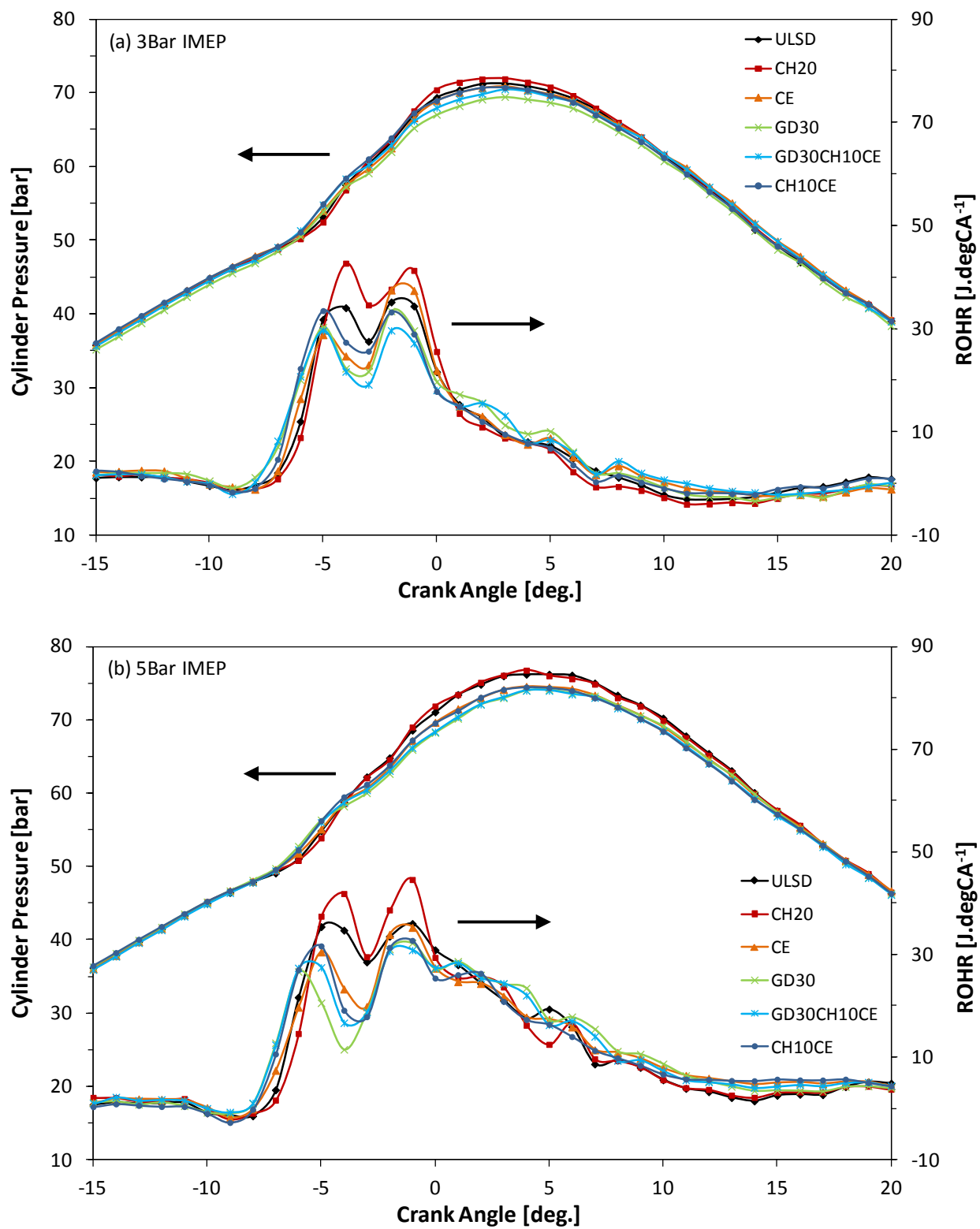


Figure 2

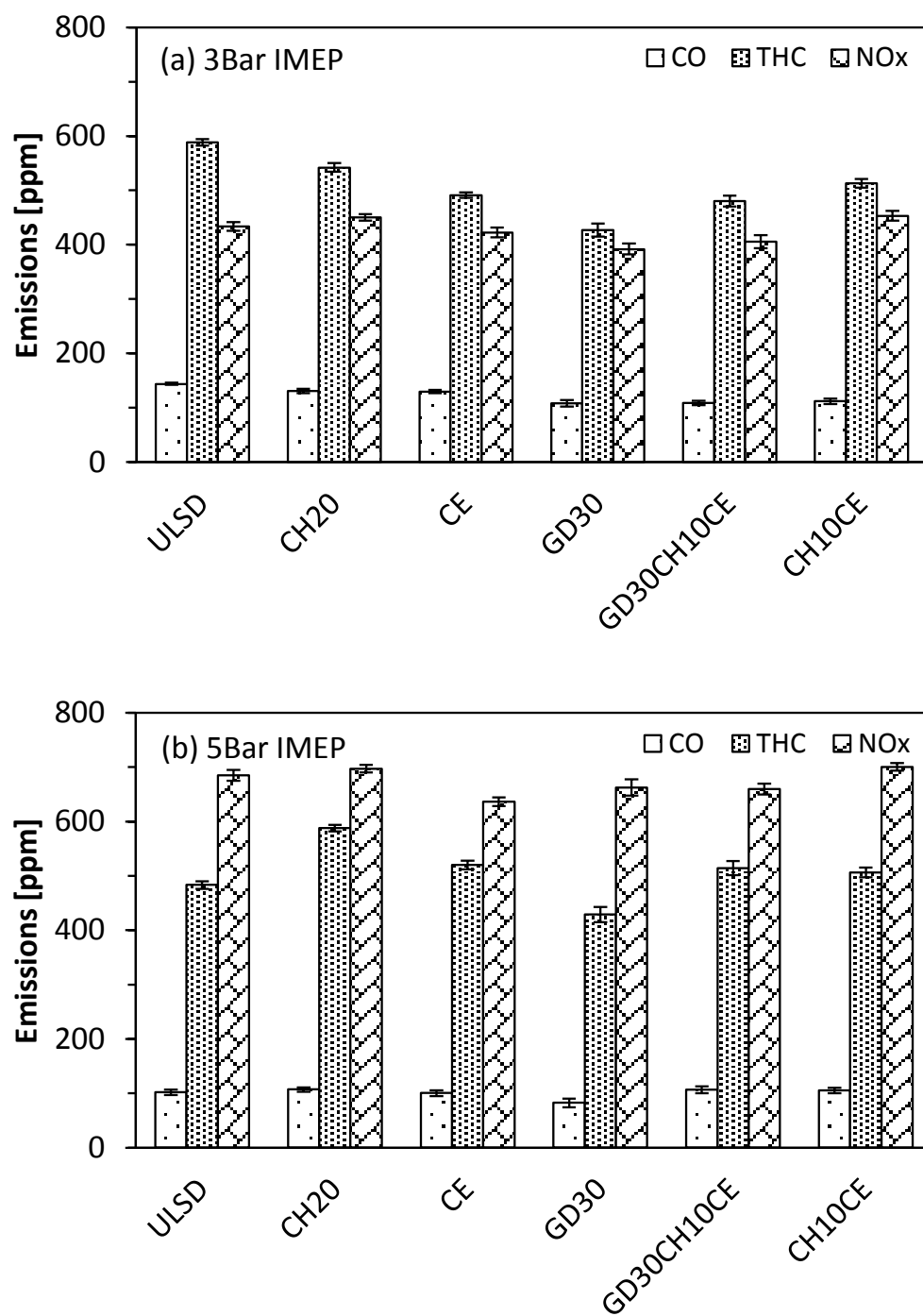


Figure 3

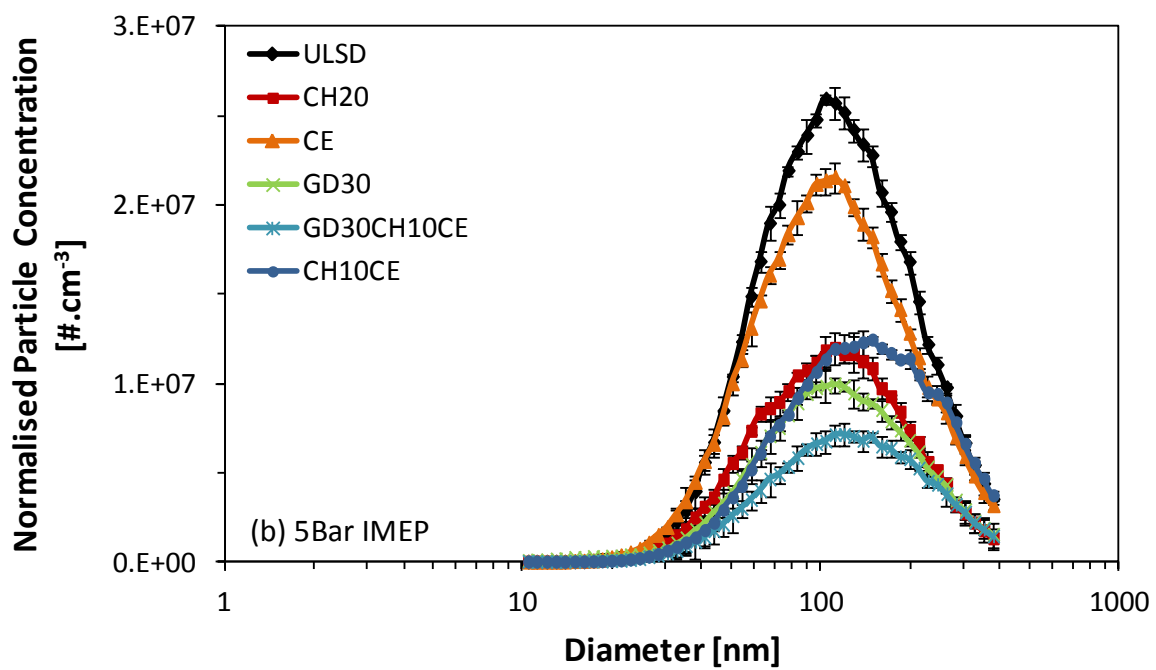
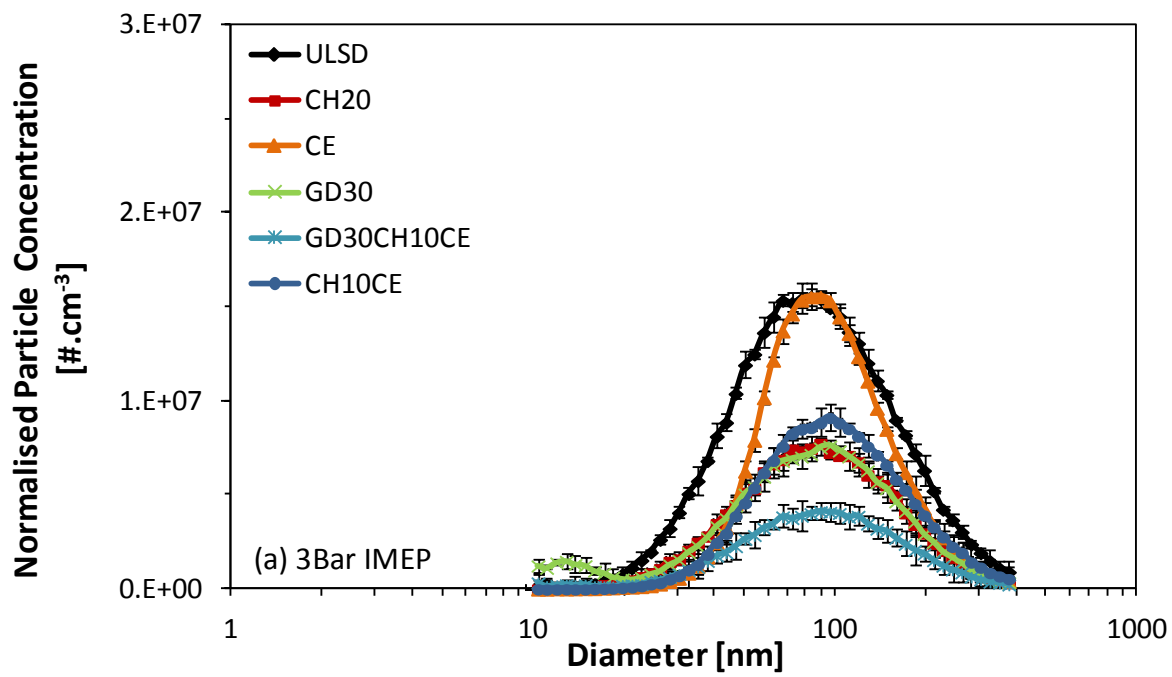


Figure 4

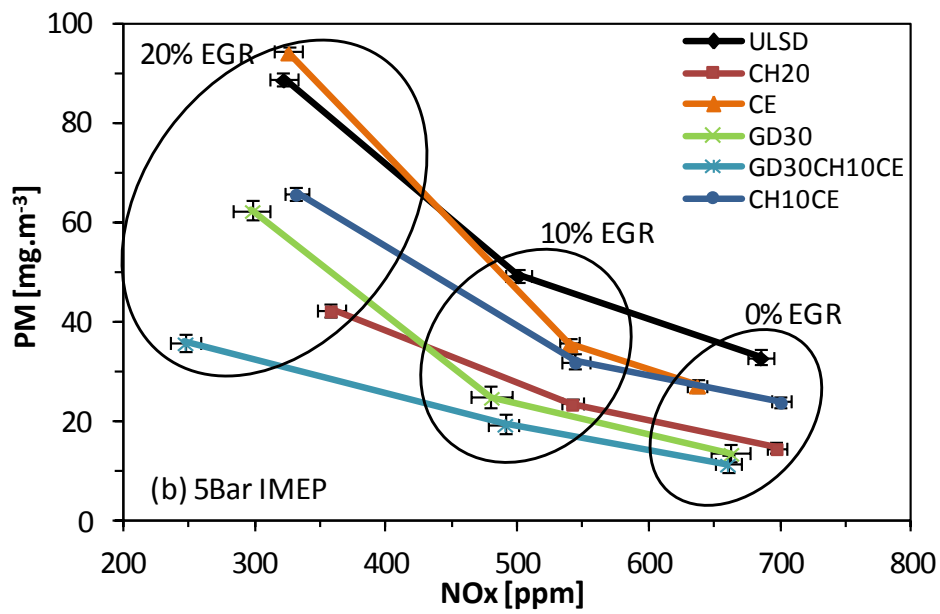
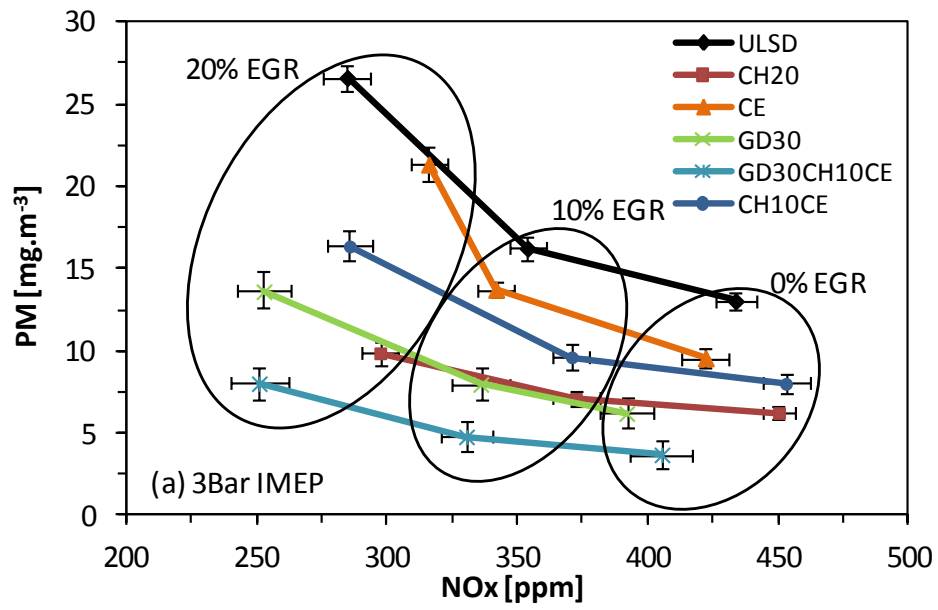


Figure 5

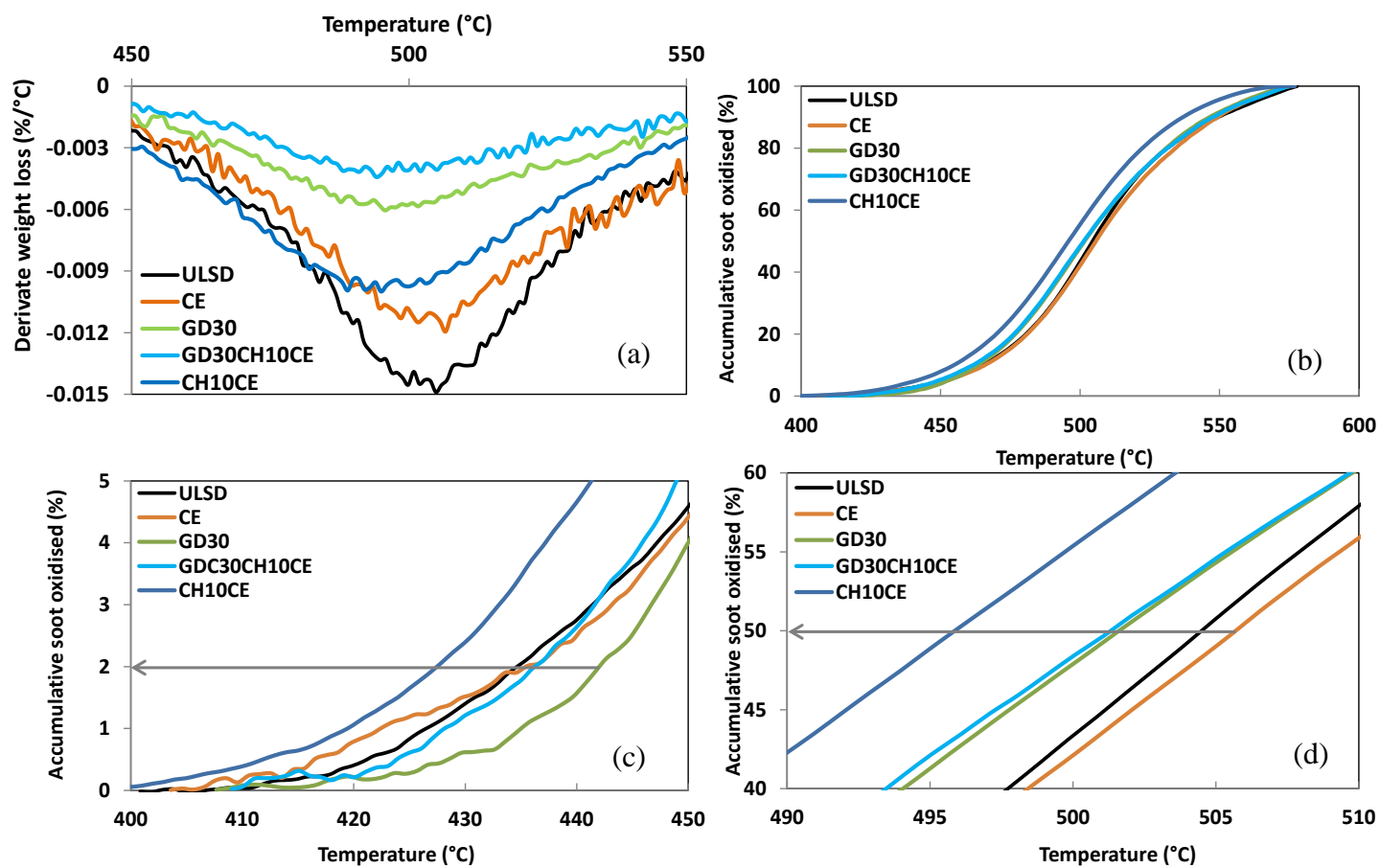


Figure 6