

Extending the environmental benefits of ethanol–diesel blends through DGE incorporation

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1 **Extending the environmental benefits of ethanol-diesel blends through DGE incorporation**

2

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7 **Abstract**

8 This research focuses on the potential use of DGE (diethylene glycol diethyl ether), as a high-cetane
9 number oxygenated additive to diesel-like fuels. Apart from evaluating its individual effects an
10 investigation of how DGE can facilitate the use of bio-ethanol in diesel engines was conducted; which
11 faces many technical difficulties, but can provide environmental advantages over biodiesel and
12 conventional diesel fuel. Four partly renewable fuel blends with varying contents of DGE and ethanol
13 were designed with overall diesel-replacement rate of 20%.

14 DGE was found to reduce gaseous emissions, achieving a simultaneous reduction in both soot and NO_x
15 which highlighted the beneficial effects of its high cetane number and oxygen content. In ethanol-diesel
16 blends small additions of DGE significantly enhanced blend stability and blend auto-ignition properties.
17 Improvements in the NO_x/soot trade-off characteristics were obtained for all blends. All tested blends
18 produced lower particulate matter number concentrations and soot with characteristics that reduced their
19 oxidation temperatures, hence providing benefits for diesel particulate filter regeneration. Overall it was
20 found that DGE provides considerable energy and environmental benefits if used both as a single
21 oxygenate with diesel or in multicomponent blends with ethanol and diesel.

22 **Keywords:** diesel combustion, ether, ethanol blends, NO_x-soot trade-off, soot oxidation

23 **Acronyms and Abbreviations**

24

CAD	Crank angle degree	LHV	Lower heating value
CO	Carbon monoxide	NO _x	Oxides of nitrogen (NO, NO ₂)
CO ₂	Carbon dioxide	PM	Particulate matter
DGE	Diethylene glycol diethyl ether	RME	Rapeseed methyl ester
DGM	Diethylene glycol dimethyl ether	ROHR	Rate of heat release
DPF	Diesel particulate filter	SOF	Soluble organic fraction
E	Ethanol	SOM	Soluble organic material
EGR	Exhaust gas recirculation	TDC	Top dead centre
FTIR	Fourier-transform infrared spectroscopy	THC	Total hydrocarbon
HC	Hydrocarbon	TGA	Thermogravimetric Analyser
HFRR	High frequency reciprocating rig	ULSD	Ultralow sulphur diesel
IETE	Indicated engine thermal efficiency	B5	Ultralow sulphur diesel +5% RME
IMEP	Indicated mean effective pressure	VOM	Volatile organic material
ISFC	Indicated specific fuel consumption		

25

26 **1. Introduction**

27 There is an increased interest in searching for alternatives energy carriers in the transportation and energy
28 generation sectors over the past decade. The motivations for that are the reduction of the fossil fuels
29 dependence (energy sustainability), a desire to reduce greenhouse gas emissions (especially CO₂ in the
30 transportation sector) and human health concerns related to other pollutant emissions (particulate matter,
31 NO_x, CO, etc.). In fact, in a recent press release, the International Agency for Research on Cancer (IARC)
32 classified diesel exhaust as carcinogenic to humans (Group 1). Due to these issues new legislation is being
33 introduced to promote the use of biofuels in the transportation sector and strict pollutant emission
34 regulations must be fulfilled demanding the incorporation of aftertreatment systems.. These short and
35 medium term scenarios indicate the ideal timeliness for research aiming to design new energy alternatives
36 able to overcome those energy and environmental issues taking into account the interaction between some
37 of the vehicle systems (e.g. the effect of alternative fuels in the diesel particulate filter).

38 Efforts to tackle these challenges have been based on both engine and fuel-focused techniques. Diesel
39 reformulation using sustainably sourced biofuels seems to be a promising field of research. The focus now
40 lies on biofuels obtained from non-edible feedstock leading to several publications critically assessing the
41 production and environmental implications of energy alternatives derived from algae [1]-[2], triglycerides
42 [3], lignocellulose [4]-[5], etc. A feasible and common alternative could be the use of primary alcohols
43 such as methanol [6], ethanol [7], butanol [8] and/or pentanol [9]. Traditionally, ethanol is the one which
44 more attention has received as it could be produced from non-edible feedstock and it has some advantages
45 over biodiesel in terms of availability, price and emission characteristics. Its oxygen content is about three
46 times higher than biodiesel resulting in further improvements in PM emissions [10]-[11] and it has been
47 demonstrated to reduce NO_x emissions under certain operating conditions [12]. However various
48 limitations in the use of ethanol in compression ignition (CI) engines exist due to its adverse effects on
49 some key fuel properties in particular flash-point [13], blend stability with diesel-like fuels, viscosity,
50 lubricity and cetane number [12]-[15]. For high ethanol content in diesel blends (i.e. e-diesel) cetane-
51 enhancing and stability-improving components must be utilised [16] such as biodiesel **Error! Reference**
52 **source not found.**-[18].

53 Diethylene glycol diethyl ether (DGE) could be a promising fuel additive for compression ignition engines
54 based on its high cetane number and its high amounts of fuel-born oxygen. These properties also qualify
55 DGE as a potential cetane-enhancing additive to e-diesel blends. A review of the limited literature
56 suggests that DGE may have similar effects to DGM, a well-studied [17]-[18] but about three-times more
57 expensive oxygenate. When combusting pure DGE under EGR conditions in a diesel engine, Cheng et al.
58 obtained reductions in all regulated emissions as compared to neat diesel [23] which was confirmed in two
59 other studies by Upatnieks et al. who attributed this to the high oxygen content and low soot formation
60 potential of DGE [24][25]. Yet the available literature on DGE fails to give a detailed account of the
61 additive's real-world potential in diesel combustion as there are no in-depth studies on its combustion
62 pattern and detailed emission characteristics. The factual novelty of this work, however, is the

63 enhancement of ethanol-diesel blends through the incorporation of DGE which has so far not been
64 attempted.

65 The aim of this investigation is to evaluate the potential of DGE as a diesel additive with a view towards
66 designing new feasible fuel blends composed of different hydrocarbon constituents to partly replace diesel
67 fuel while obtaining energy efficiency improvements and environmental benefits. In doing so the effects
68 of various fuel blends on engine performance, combustion patterns, exhaust emissions and aftertreatment
69 systems are investigated.

70 **2. Material and Methods**

71 *2.1 Test Engine and Instrumentation*

72 For this research a natural aspirated single-cylinder diesel engine was utilised. The research engine
73 employs a pump-line nozzle direct injection system with mechanical injection timing. The injector has 3
74 holes with 0.25mm diameter each, while the opening injection pressure is 180 bar. Injection timing was
75 not optimised for the different fuel blends. A Thrige Titan DC electric dynamometer with a load cell and a
76 thyristor controlled Shackleton System Drive was used to load and motor the engine.

77 Each fuel was tested at constant engine speed (1500 rpm) and two different load conditions of 3 bar and 5
78 bar indicated mean effective pressure (IMEP) representing ~30% and ~70% of the engine's power
79 capacity respectively. Additionally exhaust gas recirculation (EGR) of 0%, 10% and 20% was introduced
80 for both loads to study its effect on emissions. The results and error bars showed in the graphs are
81 calculated from three measurements for every studied fuel blend and engine operating condition. A
82 calibrated glass bulb, connected in parallel with the fuel tank, was used to determine the liquid fuel flow
83 by timing the consumption of a known volume of fuel. The volumetric fuel consumption was converted
84 into mass fuel consumption using the density values of the fuels.

85 In-cylinder pressure traces were acquired by a Kistler 6125B quartz type pressure transducer mounted at
86 the cylinder head and a Kistler 5011 charge amplifier at crank shaft positions determined by a 360-ppr

87 incremental shaft encoder with data recorded by a National Instruments PCI-MIO-16E-4 data acquisition
88 board installed in a PC. In-house developed LabVIEW based software was used to obtain pressure data
89 and combustion parameters were calculated based on 200 consecutive engine cycles after they were
90 conditioned and smoothed (e.g. coefficient of variation – COV of IMEP, peak pressure, indicated power
91 and heat release). The COV of IMEP was always below 5% and the COV of peak pressure was always
92 below 2%.

93 The apparent heat release rate was calculated using the following equation:

$$94 \quad \frac{dQ}{d\theta} = \frac{\gamma}{\gamma - 1} p \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dp}{d\theta}$$

95 Where, γ is the ratio of specific heats (Cp/CV), p is the instantaneous in-cylinder pressure and V is the
96 instantaneous engine cylinder volume. The values of γ are calculated by interpolation based on the actual
97 p-V diagrams. It is worthy to notice that in the literature there are advanced models which consider the
98 instantaneous in-cylinder composition to calculate rate of heat release and in-cylinder mean combustion
99 temperature [26]. Those advanced models has not been considered here, while they will be taken into
100 consideration for further work in order to more accurately calculate gross and net rate of heat release as
101 well as mean in-cylinder temperature.”

102 The engine exhaust emission analysis was focused on soot, PM, NO_x, THC, CO and CO₂. An in-depth
103 investigation of particulate matter (PM) was carried out. Fourier Transform Infrared (FTIR) gas analyser
104 from MKS was used to measure gaseous emissions. An additional Horiba Mexa 7100DEGR analyser was
105 employed to measure the concentrations of NO_x, CO, CO₂, O₂ and THCs. The analyser measures NO_x
106 (NO + NO₂) by chemiluminescence, CO and CO₂ are measured using non-dispersive infrared (NDIR), O₂
107 by an electrochemical method and hydrocarbons (THCs) by flame ionisation detection (FID). A Horiba
108 Mexa-1230 PM analyser was employed to determine soot, SOM (soluble organic material), SOF (soluble
109 organic fraction), and the total amount of PM in the exhaust. Secondly a TSI scanning mobility particle
110 sizer (SMPS) 3080 electrostatic classifier was used to establish the particle size distribution. The sample
111 was thermo-diluted using a rotating disk, with the dilution ratio set to 200:1 at 150°C. Finally PM was

112 collected on glass filters using an in-house ejector diluter (8:1 dilution ratio) drawing diluted exhaust gas
113 through the filter at 10 l/min for 60 min. The filters were analysed in a Perkin-Elmer Pyris 1 TGA
114 thermogravimetric analyser following the method described by Gill et al. [22].

115 *2.2 Fuel blends selection*

116 As discussed above there are some crucial fuel properties which are adversely affected by the addition of
117 ethanol (e.g. blend stability, cetane number, lubricity, etc.). Prior to choosing blend compositions for
118 engine tests these limiting factors were further investigated and compared with the applicable European
119 standard for diesel fuels EN 590:2009 [27].

120 The miscibility of DGE with ULSD and ethanol was studied by preparing multiple diesel blends with
121 different DGE contents and storing them at temperatures from +10 °C to -5 °C. Previous research into the
122 stability of diesel-ethanol blends concluded that blends of ULSD and 20% ethanol become unstable at
123 temperatures below 20 °C [8]. In this work the beneficial effects of the DGE on ethanol-diesel blend
124 stability was investigated. The incorporation of 5% DGE enables to obtain stable 20% ethanol - diesel
125 blends at temperatures as low as -5°C. The minimum and maximum viscosity limits are 2.00 and 4.50 cSt
126 respectively. Referring to Table 1 it is apparent that this limit is not infringed by the replacement of just
127 20% of the base fuel with DGE or ethanol. Lubricity was measured using a PCS Systems High Frequency
128 Reciprocating Rig (HFRR). The corrected wear scar diameter obtained in this test must not exceed 460
129 µm [28]. Earlier investigations indicated that blends with DGE content above 15% exceeded this
130 permitted limit. The incorporation of ethanol in these blends is expected to reduce blend lubricity further
131 due to the poor lubricity properties of ethanol [14]. This would result in overall diesel replacement rates of
132 just around 10%. To overcome this limitation 5% of Rapeseed methyl ester biodiesel (RME) was added to
133 the diesel fuel (subsequently called B5) in order to improve the lubricity of alcohol-diesel blends [29]-
134 [30]. Further tests confirmed that this small addition of RME eliminates the problem of lubricity for diesel
135 replacement rates with ethanol of up to 30% (see Figure 1).

136 In line with the research aim and objectives four blends were prepared. To study the effects of DGE on
137 combustion and emissions a DGE-B5 blend was prepared. To investigate how DGE can improve e-diesel
138 blends three tertiary blends with varying contents of DGE and ethanol were created. For all four blends
139 the overall diesel replacement rate was 20%. While the ethanol content was increased step by step in
140 increments of 5%, the DGE content was decreased stepwise by the same percentage. As a result, the total
141 oxygen content was at similar levels for the blends, diminishing the total oxygen content effect when
142 blends are compared. The four test blends were compared with the B5 reference fuel. ULSD, RME and
143 Ethanol were obtained from Shell Global Solutions (UK) while DGE was sourced from Sigma-Aldrich.
144 Relevant fuel properties have been measured and/or found in the relevant literature [29], [31]-[33] as it is
145 detailed in Table 1. It was again verified that the aforementioned key blend properties complied with the
146 standard.

147 **3. Results and Discussion**

148 *3.1 Performance Parameters*

149 Figure 2 (a) shows the indicated thermal efficiency (ITE), the ratio of the engine's indicated power output
150 to the flow fuel's energy content (mass fuel consumption times fuel's lower heating value). On one hand,
151 the fuel consumption is increased for all blends as compared to the B5 reference fuel. On the other hand,
152 the heating value of the blends is lower than the heating value of B5. The increased in specific fuel
153 consumption for the blends are lower than the decrease in heating value [34] slightly increasing indicated
154 thermal efficiency. Studies have shown that this increase is mainly due to the oxygenated nature of the
155 fuel additives [35]. The increased oxygen availability achieves a more complete combustion even in fuel-
156 rich regions. Additionally it can be seen that all blends achieve nearly identical efficiencies which seems
157 to confirm the correlation between oxygen mass fraction and thermal efficiency as described in prior
158 studies.

159 *3.2 Combustion Characteristics*

160 In Figure 2 (b) the in-cylinder pressure and rate of heat release (ROHR) for the operating load of 3 bar
161 IMEP are plotted against the crank angle degree for 0% EGR. The shortest ignition delay was observed
162 for 20DGE followed by 15DGE5E, B5, 10DGE10E and finally 5DGE15E. The start of combustion of the
163 5DGE15Ethanol blend is 6CAD bTDC, when ethanol is substituted by DGE for the 10DGE10Ethanol and
164 15DGE5Ethanol the start of combustion is advanced to 7 and 8CAD bTDC, respectively. This behaviour
165 qualitatively follows the differences in estimated cetane numbers [36],[37] when fuel molar fractions are
166 considered. However, when cetane number estimation is based on mass fraction, all the fuel blend's
167 cetane values are higher than those of B5 which does not correspond to the delay time experimentally
168 observed. The above discussed results, lead to conclude that the estimation based on molar fraction better
169 reflects the autoignition properties of a multi-fuel blend when the components have very different
170 molecular masses (e.g. ethanol, diesel and DGE).

171 The combustion process is generally characterised by an initial pre-mixed combustion (the first heat
172 released peak [38]) followed by a diffusion combustion phase [39]. The intensity of these phases varies
173 considerably across the different blends. The 5DGE15E-blend has the largest pre-mixed combustion phase
174 resulting in the largest heat release peak. The long ignition delay allows the fuel to mix well with the air
175 leading to a more homogenous initial combustion [38]. 20DGE has the smallest premixed combustion
176 phase for both load conditions due to its short ignition delay. Also, as has been concluded in various
177 studies under similar mode of combustion the higher the degree of premixed combustion, the higher the
178 peak pressure [23],[38]. This is the case for the 3 bar condition and applies also to the 5 bar condition.

179 *3.3 Gaseous Carbonaceous Emissions*

180 The THC emissions of all blends at both engine operating loads (Figures 3 and 4) are lower than those of
181 B5. This can be attributed to the higher oxygen content of the fuels which causes a cleaner and more
182 complete combustion [6],[34],[40]. 20DGE and 15DGE5E show the lowest overall THC emissions while
183 the THC emissions of 5DGE15E are the highest of the studied blends. The increase of hydrocarbon
184 emissions when ethanol is used it has been previously reported in the literature [14],[17],[18],[31]. The

185 main reasons for the higher unburnt hydrocarbon emissions when the ethanol content is higher could be i)
186 the higher cetane number of these blends that lead to an advanced combustion resulting in more available
187 time to completely oxidise hydrocarbons and CO [34],[41] ii) the high enthalpy of vaporisation of ethanol
188 which will result in a reduction in the in-cylinder combustion temperature inhibiting the hydrocarbon
189 oxidation [31]. The specific THC emissions are generally lower at high loads. This is most likely due to
190 increased peak pressures resulting in a more complete combustion.

191 CO emissions demonstrate a very similar qualitative behaviour to THC emissions. Again the results can
192 be explained by referring to oxygen content, enthalpy of vaporisation and cetane number. The emissions
193 for three of the four blends are clearly reduced as compared to B5 at both 3 bar and 5 bar IMEP due to
194 their higher oxygen content [22],[23],[38]. The 5DGE15E blend produced higher CO emissions than B5.
195 This is thought to be a result of its lower cetane number and consequently retarded combustion phasing.
196 Various studies into the field have found that lower cetane numbers tend to increase CO emissions, an
197 effect which has been attributed to the resulting retarded combustion allowing less time for the fuel and
198 intermediate species to combust completely [42],[43]. For this blend the negative effects of a lower CN
199 number seem to outweigh the positive effects of increased oxygenation in terms of CO emissions.

200 *3.4 Nitrogen Oxides (NO_x) Emissions*

201 NO_x emissions for the studied blends compared to B5 are shown in Figure 3 and 4. To explain the
202 different trends across the studied blends four main factors are considered: fuel-born oxygen, ignition
203 delay, the ratio of premixed to diffusion combustion and the enthalpy of evaporation.

204 It has been previously reported that the presence of fuel-born oxygen could increase NO_x emissions. The
205 oxygen in the fuel could promote the NO formation reaction [34],[44] and reduce the heat losses by soot
206 radiation resulting in higher in-cylinder combustion temperature [34],[42]. Furthermore, the larger
207 premixed combustion phase resulting in higher peak pressures and temperatures also promote NO_x
208 formation. These two factors could explain why the combustion of two of the four blends (15DGE5E and
209 10DGE10E) show significantly higher emissions of NO_x than the combustion of B5 and rest of the tested

210 fuel blends. However, the 5DGE15E blend exhibits a decrease in NO_x emissions compared to 10DGE10E
211 although its premixed phase is larger. A possible explanation is the higher ethanol content in the blend.
212 Ethanol has a high enthalpy of evaporation causing temperatures to decrease during combustion [31]. This
213 effect seems to counteract the influence of the premixed combustion and higher oxygen content for this
214 blend while it seems not to be strong enough in the blends containing only 5% and 10% of ethanol. In the
215 case of 20DGE, the lower premixed-to-diffusion-combustion ratio is the dominant factor leading to lower
216 peak pressures (as can be observed in Figure 2 (b)) and thus lower NO_x levels.

217 *3.5 Particulate Matter (PM) emissions and their composition*

218 Particulate Matter is composed of two main fractions: i) soot which is solid carbonaceous material and ii)
219 soluble organic material which are adsorbed/condensed hydrocarbons onto the soot particles' surface [45]
220 (PM = Soot + SOM). The SOF is defined as the proportion of SOM in total PM (SOF = SOM/PM).

221 In addition to the gaseous emissions, soot results can be found in Figures 3 and 4. It can be seen that all
222 four blends show reductions in soot emissions for both engine loads. The most important reason for this is
223 the increased oxygenation of the fuels [12],[22],[31],[34]-[35]. Increased oxygen availability means better
224 and more complete fuel combustion even in fuel-rich regions and promotes the oxidation of already
225 formed soot [34]. However oxygen content cannot be the only determinant of soot as the absolute soot
226 reductions vary across the blends although their oxygen mass fractions are nearly the same. To explain
227 why 20DGE has one of the smallest soot emissions the effect of DGE as an ether must be considered.
228 Westbrook et al. [46] have suggested that ethers strongly inhibit soot emissions due to their atomic
229 structure in which one oxygen atom is bonded to two carbon atoms. This way less carbon atoms are
230 available for soot production. Another crucial factor in soot emissions is the ignition delay of a fuel. A
231 retarded combustion tends to increase soot as there is less time for soot oxidation which is especially the
232 case for the 10DGE10E blend. However, for the 5DGE15E blend the negative effects of an even further
233 retarded combustion as well as much lower ether content seem to be outweighed by the positive effect of a
234 much longer premixed combustion phase. Better premixing tends to eliminate fuel rich regions where soot

235 is primarily produced. As a result soot emissions for 5DGE15E are lower than in the case of B5,
236 15DGE5E and 10DGE10E at both operating pressures.

237 In terms of PM composition, in Figure 5 it can be observed that 20DGE has the highest SOF closely
238 followed by 5DGE15E. The increase in SOF is mainly driven by the low level of soot associated with the
239 combustion of those blends (see Figure 3 and 4) rather by a higher emission of volatile organic material
240 (VOM). However, 15DGE5E and 10DGE10E display similar SOF with respect to B5 although their soot
241 emissions are lower which can be explained by a simultaneous reduction in SOM and soot and thus an
242 overall reduction in total PM as compared to B5. When comparing engine load and EGR, SOF decreases
243 with an increase in engine load and EGR. This is again due to an increase in soot emissions derived from
244 the combustion at high engine load and EGR levels.

245 *3.6 NO_x/Soot Trade-off under EGR conditions*

246 NO_x and soot emissions for different EGR operating conditions are depicted in Figure 6. As can be seen
247 EGR reduces NO_x but increases soot (trade-off) mainly due to the decreased oxygen availability in the
248 combustion chamber. It is apparent that all blends display improved trade-off characteristics as compared
249 to B5 as they lie below the B5 trade-off curve, with 20DGE and 5DGE15E appears to have the best trade-
250 off relationship. Trade-off improvements with fuel blends (as indicated by the slope of the lines) seem to
251 be best for low EGR additions (eg. 10%). Higher EGR percentage further reduces NO_x emissions,
252 however the incurred soot penalty is much higher (higher slope of the line from 10 to 20% EGR in
253 comparison to the slope from 0 to 10% EGR) as a result of the soot recirculation penalties [47]. It follows
254 that for the tested fuels moderate levels of EGR are more favourable than higher rates.

255 *3.7 Particle Size Distribution*

256 Particle size distributions in number and mass concentration, total particle number and mean diameter size
257 are shown in Figure 7 (a), (b), (c) and (d), respectively. The particle mass distribution was obtained from
258 the particle number distribution using a size-dependant agglomerate density function as described by

259 Lapuerta et al [48]. The particle number concentration for B5 is the highest for all studied conditions. In
260 fact the order of particle number emissions from highest to lowest exactly mirrors the order obtained for
261 the soot emissions (see Figure 3 and 4). The decreased particle numbers for the oxygenated blends are
262 often associated with the increased oxygen content that promotes particle precursors and particle oxidation
263 [14][22],[31],[49]-[50] while the individual differences in particle numbers between the four blends can be
264 explained by the same reasons as for the differences in soot emissions outlined above. As can be observed
265 in Figure 7 (d), EGR greatly increases the number of particles and especially the proportion of larger
266 particles as a result of lower oxygen availability and higher particle agglomeration. This increase is more
267 noticeable in the case of B5 combustion compared to the oxygenated blends combustion. The oxygen
268 contained in the fuel is more effective in fuel-air rich conditions (as those corresponding to high EGR
269 rates) limiting particle formation as well as the particle recirculation penalty associated to high EGR rates
270 [51].

271 Figure 7 (c) indicates that the mean particle diameter is smaller for the oxygenated blends. This has often
272 been considered as one of the key drawbacks of oxygenated fuels. Smaller particles are more difficult to
273 trap, they can penetrate the respiratory and even circulatory system, they remain airborne in the
274 atmosphere for much longer than larger particles and they are more reactive due to their higher surface-to-
275 volume ratio [14]. However, Figure 7 (a) indicates that the main reason for a reduction in mean particle
276 diameter is a reduction in larger particle concentration [14],[22] which is also confirmed in the particle
277 mass distributions. Therefore lower mean particle sizes for oxygenated blends are not actually a drawback
278 but merely represent a reduction in larger particle emissions. This is a result of the lower particle
279 formation and a corresponding lower likelihood of particle collision and the formation of larger particulate
280 matter agglomerates.

281 *3.8 Soot Oxidation Analysis*

282 Soot oxidation is relevant in modern diesel after-treatment technology which involves the installation of
283 diesel particulate filters (DPF). DPFs require active regeneration to maintain their function which incurs

284 significant fuel penalties. During these cleaning cycles the filter is heated and the accumulated soot is
285 oxidised and dissipated as CO₂. In this research the oxidation temperature as well as the required
286 activation energy of the produced soot particles is estimated using a TGA. The collected particulate matter
287 samples were first devolatilised by vaporising the adsorbed volatile organic material to isolate the soot
288 effects. After cooling down the sample, the temperature is increased in an oxidant atmosphere to study the
289 soot oxidation process. From the weight loss curve the temperature at which the maximum rate of soot
290 oxidation occurs as well as the required soot activation energy can be calculated. For this purpose the
291 method outlined by Rodríguez-Fernández et al. [42] was used which involves determining the activation
292 energy from the following equation:

$$293 \quad \ln \left(\frac{dm}{m dt} \right) = \ln (A p_{O_2}) - \frac{E_a}{RT} \quad \text{Eq. (1)}$$

294 where m is the mass of soot, t the time, A is the pre-exponential factor, p_{O₂} is the partial pressure of oxygen,
295 R is the gas constant, T the temperature and E_a the activation energy.

296 Figure 8 (a) shows that the peak weight loss for B5-derived soot occurs at slightly higher temperatures
297 than for soot produced by any of the oxygenated blends. This observation is confirmed in Figure 8 (b)
298 which depicts the temperature for maximum rate of soot oxidation (second derivative of weight loss equal
299 to zero). Additionally it can be seen that considerably less soot was produced in the combustion of 20DGE
300 and 5DGE15E which qualitatively confirms the results obtained in the previous sections. Furthermore, the
301 activation energy to oxidise the soot is also lower in the case of the oxygenated fuel blends. One of the
302 reasons for this lower activation energy and soot oxidation temperature experienced for the oxygenated
303 fuel blends may be the smaller amount of large soot particles which are less reactive and thus more
304 difficult to oxidise. In addition, the potential presence of surface oxygen in the soot particles produced
305 under the combustion of oxygenated fuels has also been reported to ease soot oxidation. Further details on
306 this explanation can be found in a study by Song et al [52]. The lower soot and particulate matter emission
307 level, the lower temperature for soot oxidation and the lower soot activation energy for oxidation obtained
308 with the oxygenated blends will result in less frequent and more efficient DPF regeneration reducing the
309 associated fuel penalty.

310 **4. Conclusions**

311 In this study the applicability of DGE as an oxygenated additive and a miscibility- and cetane-enhancer in
312 ethanol-diesel blends was investigated. It was found that blends with up to 20% DGE content could be
313 created that conform with existing diesel fuel standards as long as 5% RME was added to the base fuel
314 ULSD (B5) as a means of improving the lubricity of the blend.

315 Adding DGE to diesel fuel resulted in improvements in all measured emissions compared to the B5
316 reference fuel. It should be emphasised that both soot and NO_x reductions were obtained simultaneously.
317 While the fuel-born oxygen reduced soot emission, improvements in NO_x were obtained as a result of a
318 lower premixed combustion. It can be also established that DGE improves some of the major
319 shortcomings of e-diesel. Small additions of DGE greatly enhance blend stability and improve the auto
320 ignition properties of the resulting blend due to its high cetane number. All blends produced reductions in
321 PM number concentrations and displayed improved soot oxidation behaviour which provides benefits for
322 DPF regeneration.

323 It can be concluded that in this research various partly renewable diesel blends can provide considerable
324 environmental and energy efficiency improvements while offering flexible combustion patterns. 20DGE
325 displayed the best overall emission characteristics with reductions in all investigated emissions while
326 5DGE15E followed with a similarly favourable soot/ NO_x trade-off. However differences in fuel
327 properties (e.g. lubricity), combustion patterns, price and the share of renewable blend components exist
328 between the two blends. Ultimately, the choice of which blend to use lies with the end-user and depends
329 on the specific combustion requirements.

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Table

Table 1: Fuel properties

	Test Method	B5	DGE	Ethanol	20DGE	15DGE5E	10DGE10E	5DGE15E
Chemical Formula		$C_{14.18}H_{26.42}O_{0.07}$	$C_8H_{18}O_3$	C_2H_6O	$C_{12.63}H_{24.31}O_{0.81}$	$C_{11.08}H_{21.56}O_{0.72}$	$C_{9.85}H_{19.37}O_{0.65}$	$C_{8.85}H_{17.58}O_{0.59}$
Molar mass [g/mol]		197.76	162 140 Error! Reference source not found.	46	186.12	163.69	145.85	131.34
Cetane Number ^a		53.94	140 Error! Reference source not found.	8 ^[29]	71.18	68.89	62.29	55.69
Cetane Number ^b		53.93	found.	8 ^[29]	75.49	60.46	48.52	38.80
Viscosity at 40 °C [cSt]	ISO 3105	2.57	1.18	1.13 ^[31]	2.27	2.28	2.29	2.29
Density at 15 °C [kg/m ³] ^c	ISO 12185	829.87	908 ^[32]	789 ^[31]	845.70	827.70	833.70	839.70
LHV [MJ/kg] ^a	ISO 1928	42.99	31.40	26.83 ^[33]	40.50	40.35	40.19	40.04
Lubricity at 60 °C [μm]	ISO 12156-1	294	747	656	431	414	411	403
C [wt%]		86.02	59.26	52.17	80.57	80.39	80.20	80.02
H [wt%]		13.40	11.11	13.04	12.97	13.07	13.18	13.29

O [wt%]	0.58	29.63	34.78	6.46	6.54	6.62	6.70
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^a estimated based on mass fraction
^b estimated based on molar fraction
^c estimated based on volumetric fraction

Figure Captions

Figure 1: Corrected wear scar of DGE-ULSD blends, DGE-B5 blends and the test-blends

Figure 2: (a) Indicated engine thermal efficiency, (b) cylinder pressure and ROHR for 5 bar IMEP and 0% EGR

Figure 3: Emissions at 3 bar IMEP (a) 0% EGR, (b) 20% EGR

Figure 4: Emissions at 5 bar IMEP and (a) 0% EGR, (b) 20% EGR

Figure 5: Soluble Organic Fraction (SOF) for all operating conditions

Figure 6: NO_x/Soot trade-off under EGR conditions (5 bar IMEP)

Figure 7: Fuel effects on (a) particle size distribution, (b) mass distribution, (c) total particle number and mean diameter at 0% EGR and 5 bar IMEP, (d) total particle mass with varying EGR

Figure 8: (a) Derivative dry soot weight loss, (b) oxidation temperature and soot activation energy (E_a) at 5 bar IMEP and 0% EGR

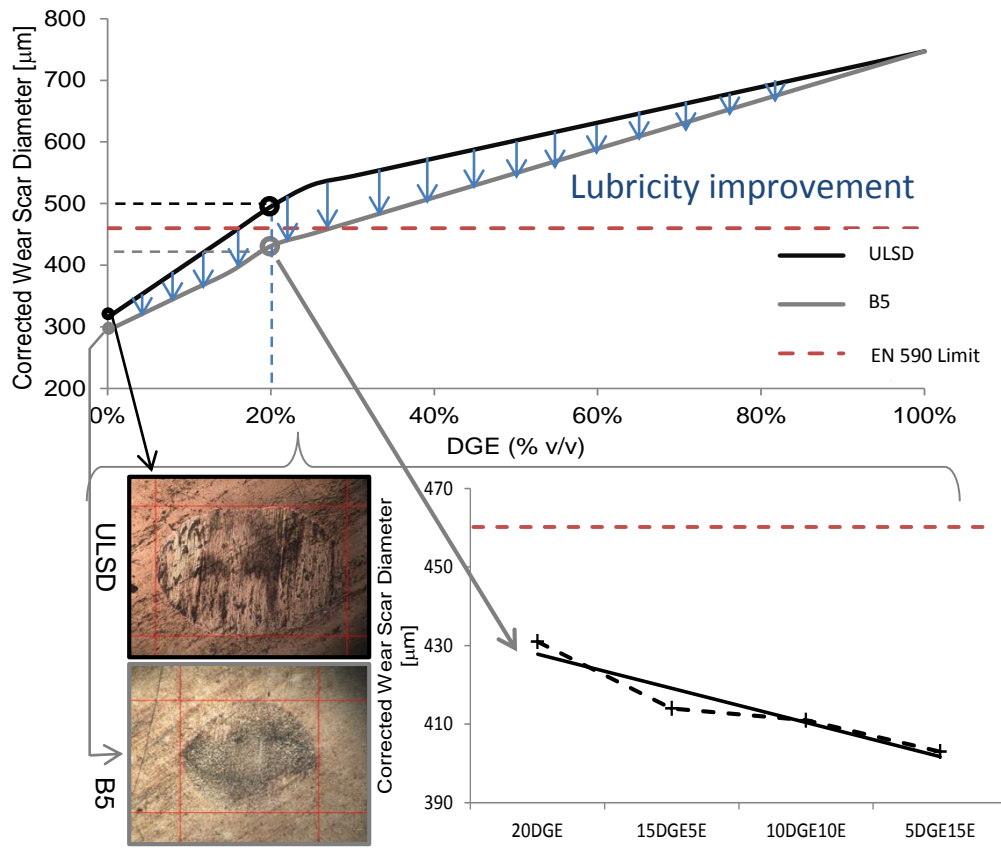


Figure 1

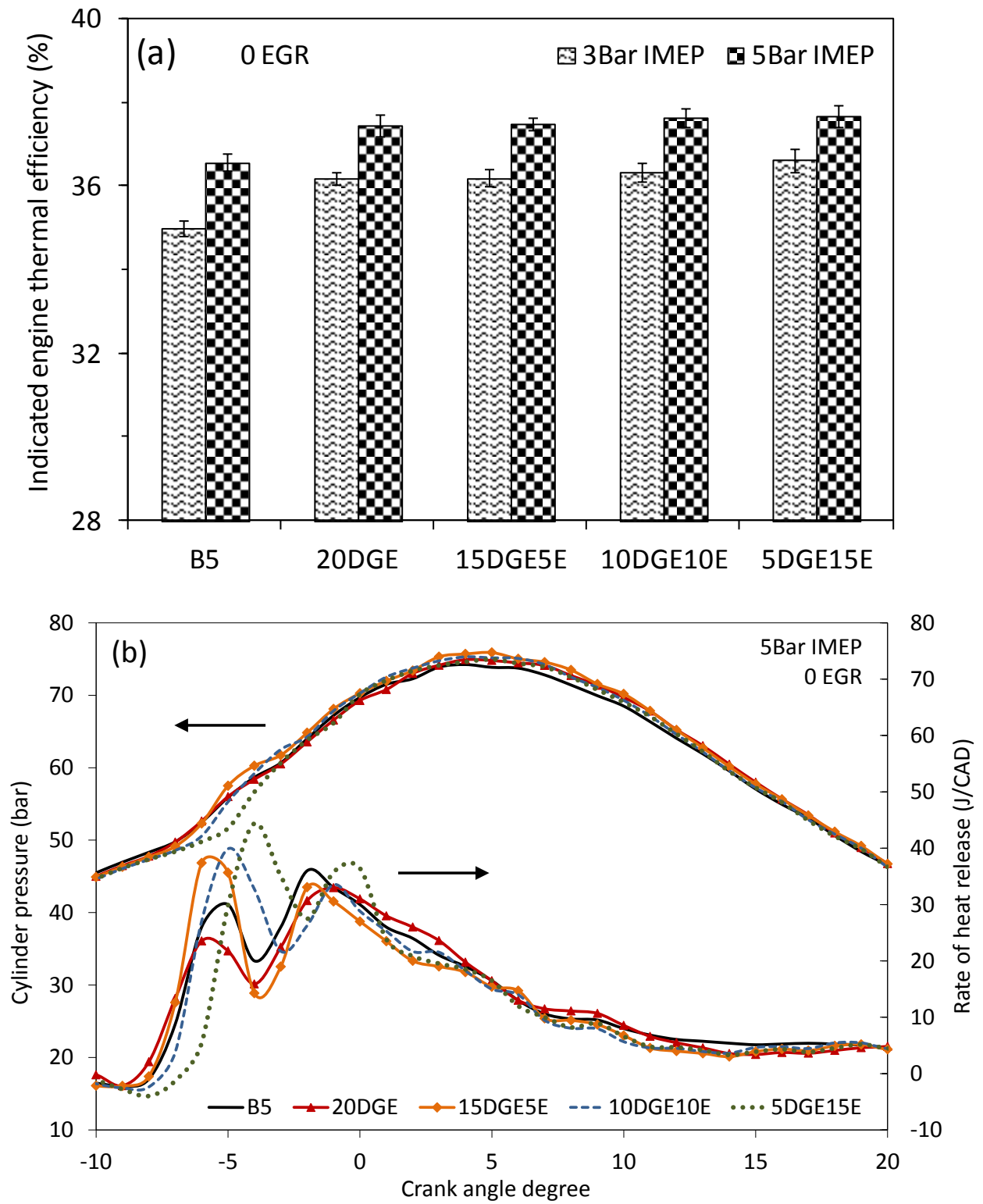


Figure 2

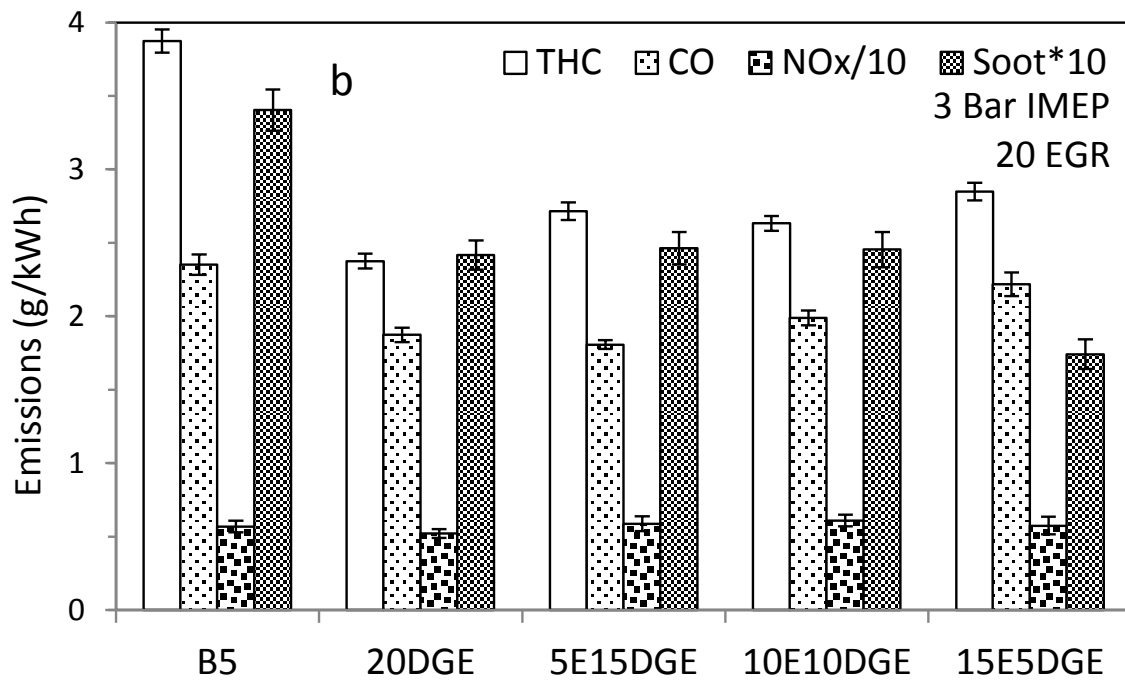
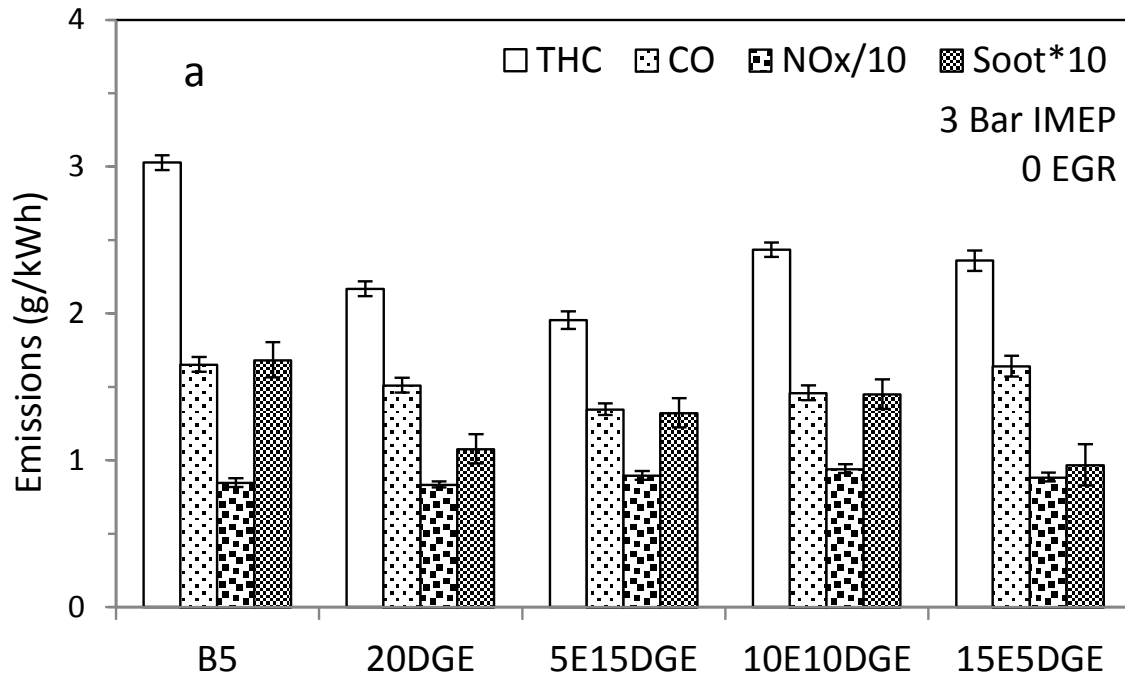


Figure 3

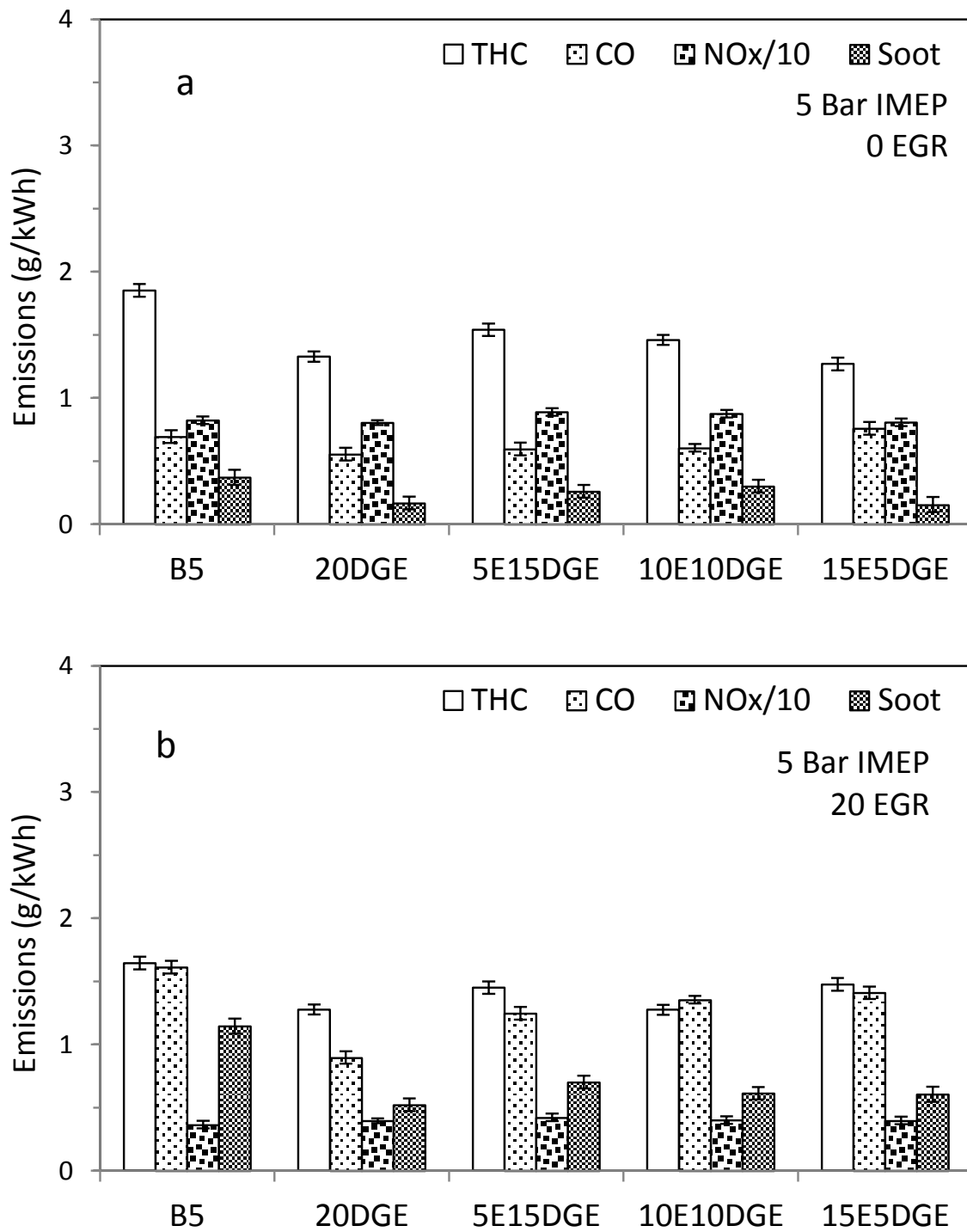


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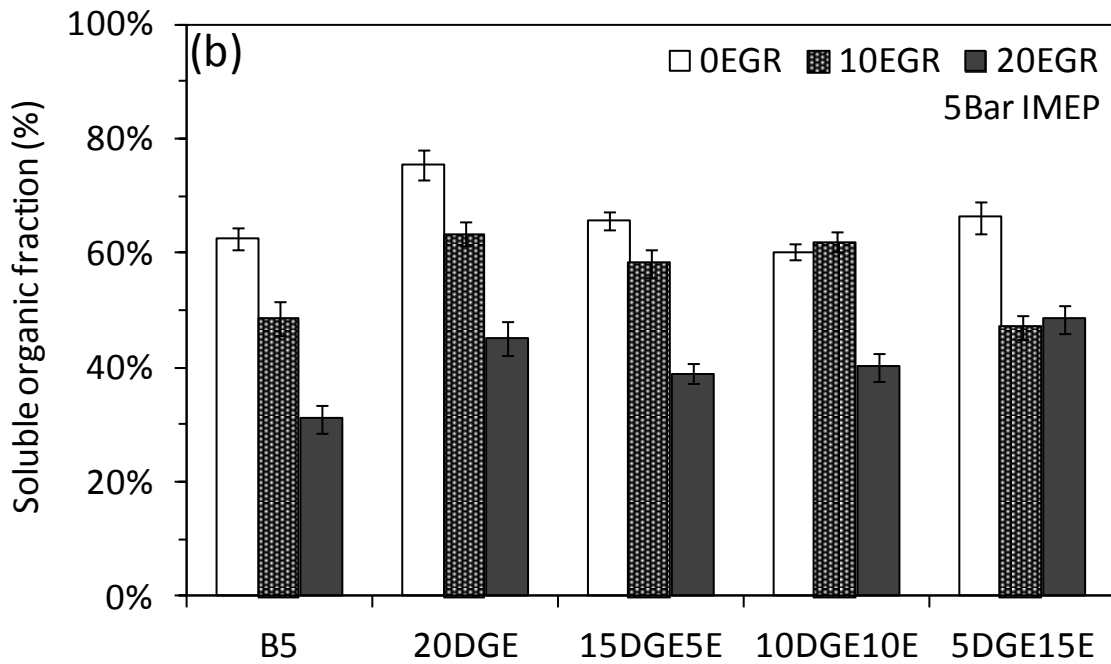
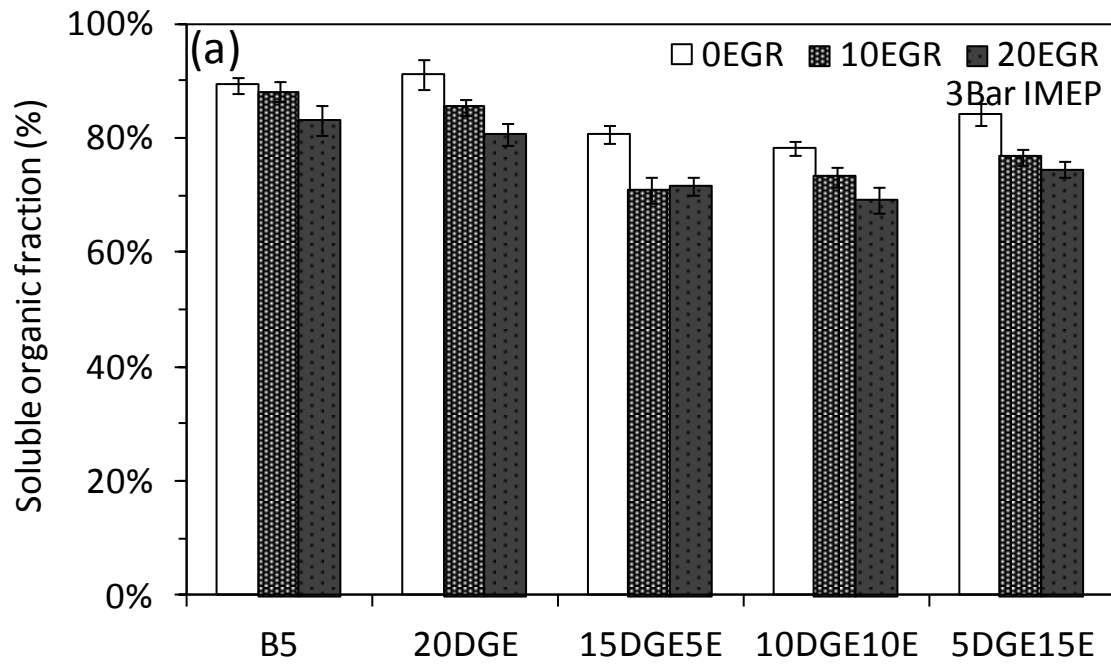


Figure 5

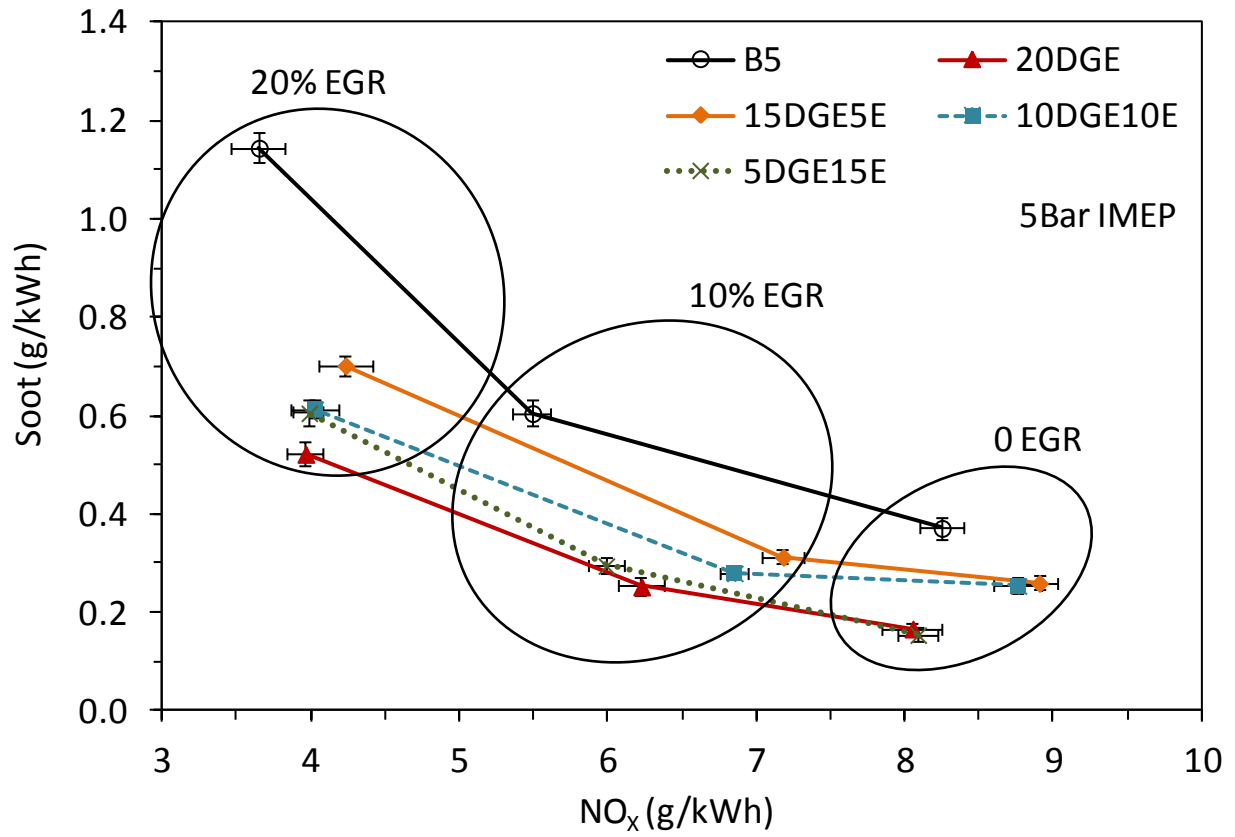
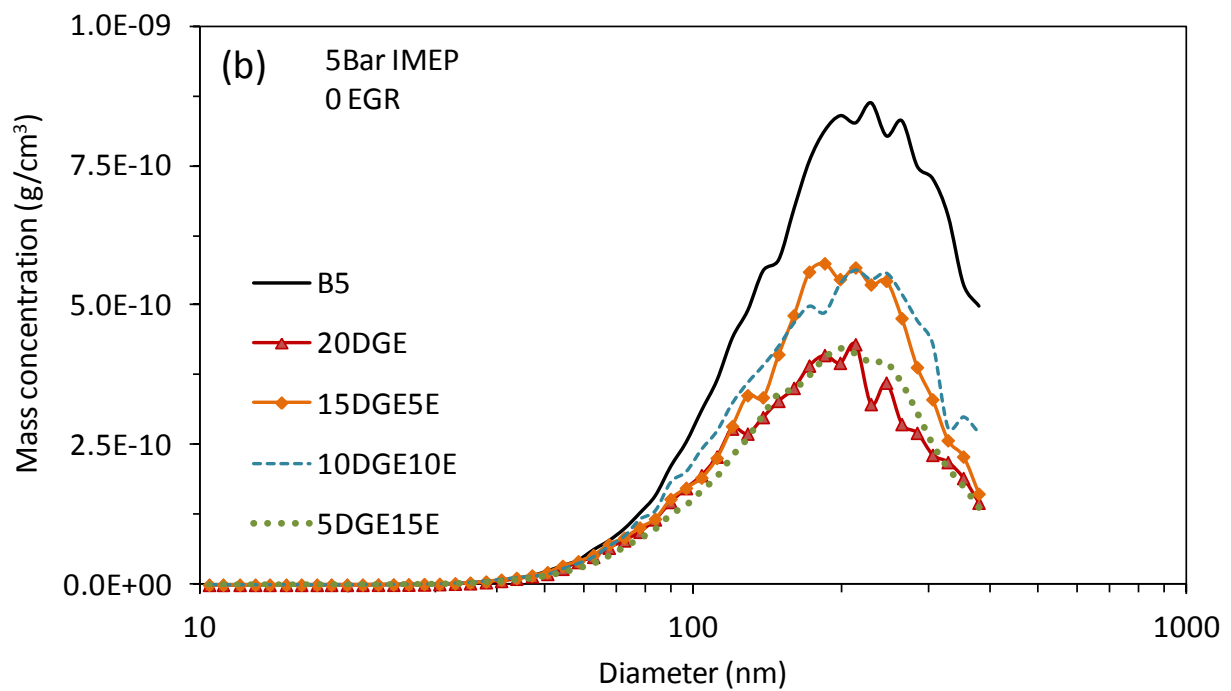
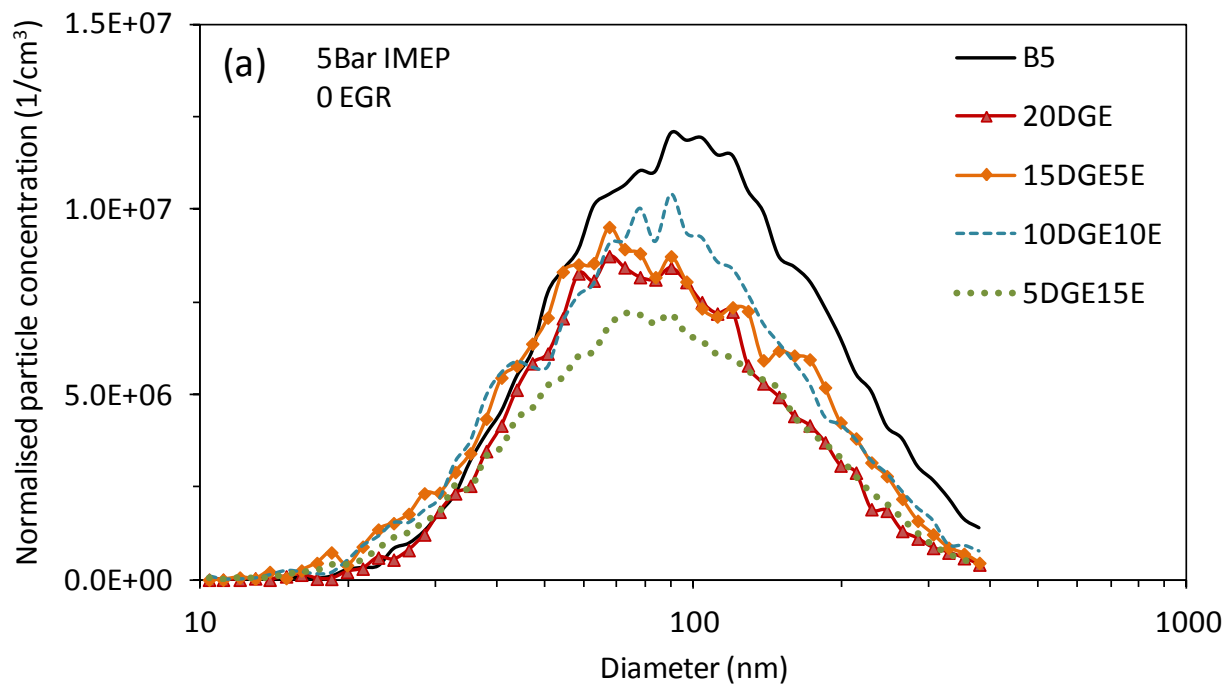


Figure 6



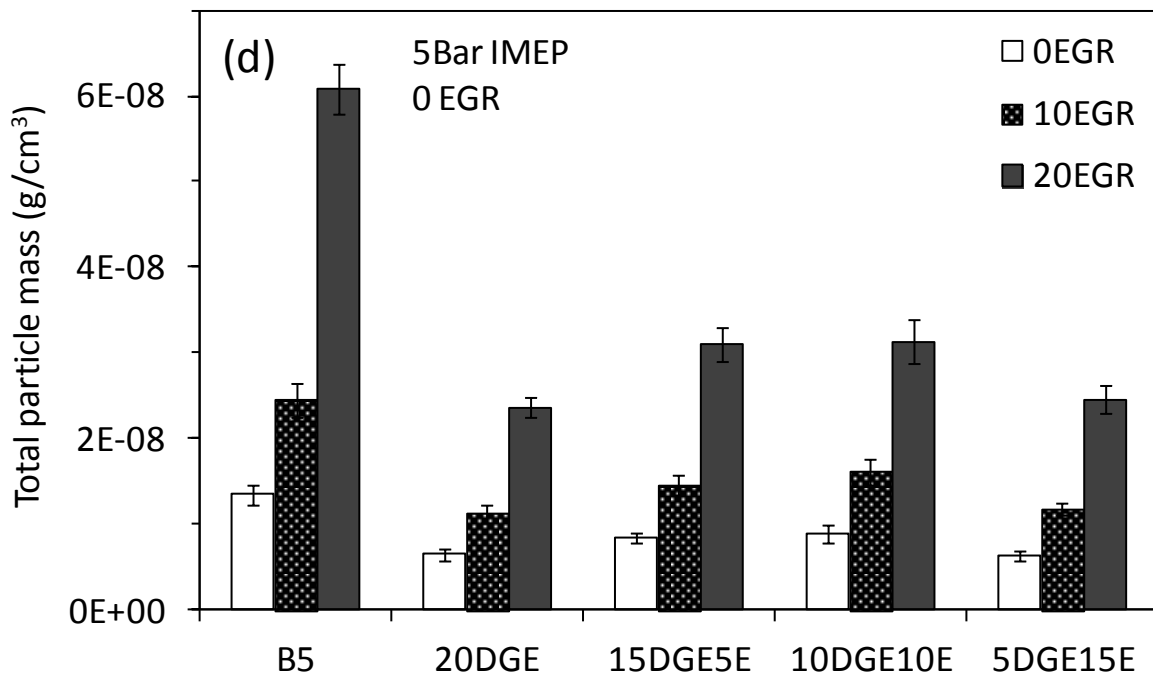
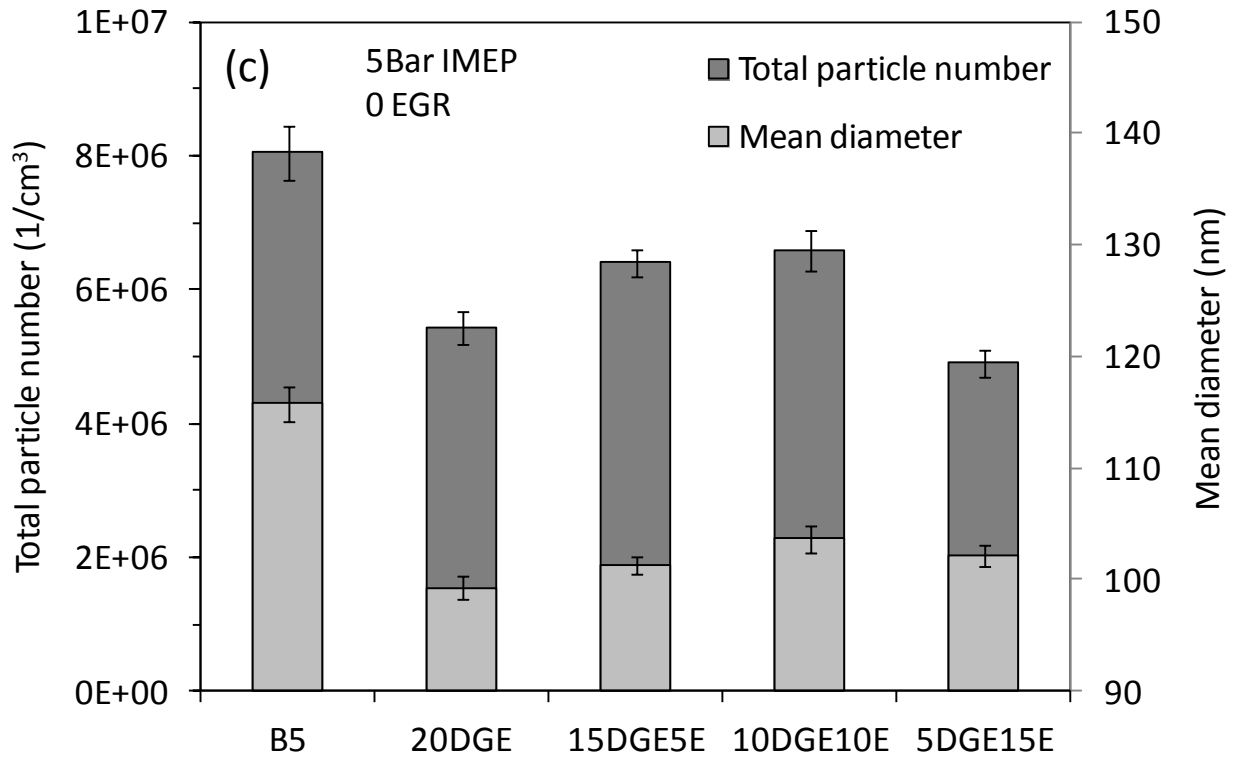


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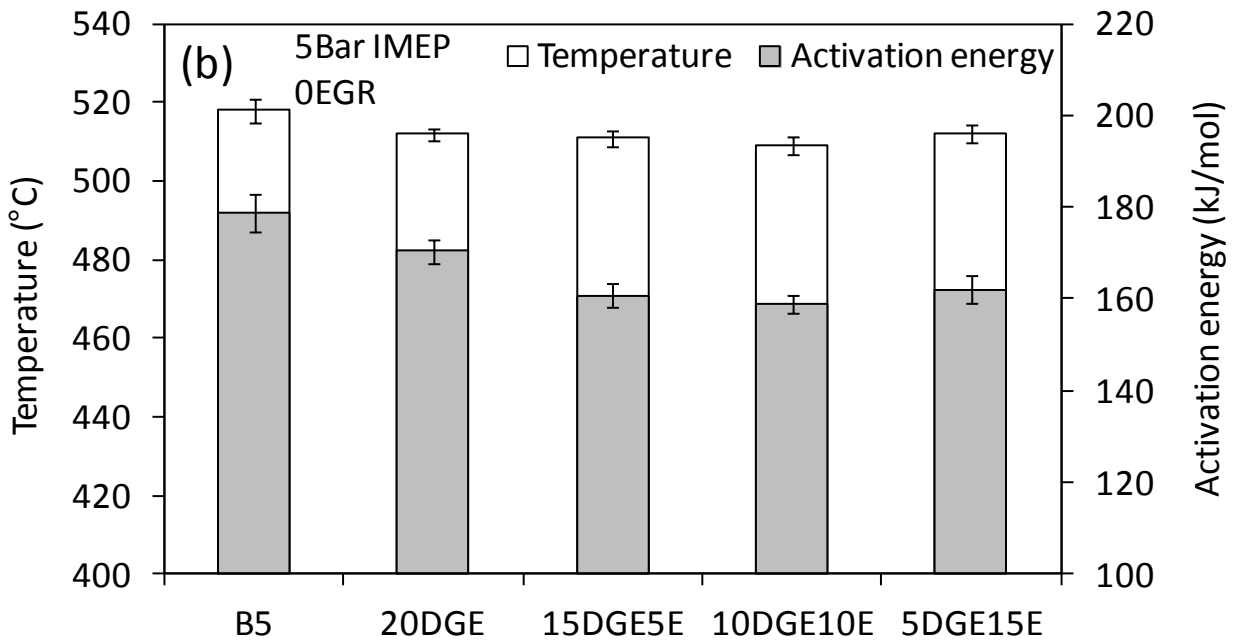
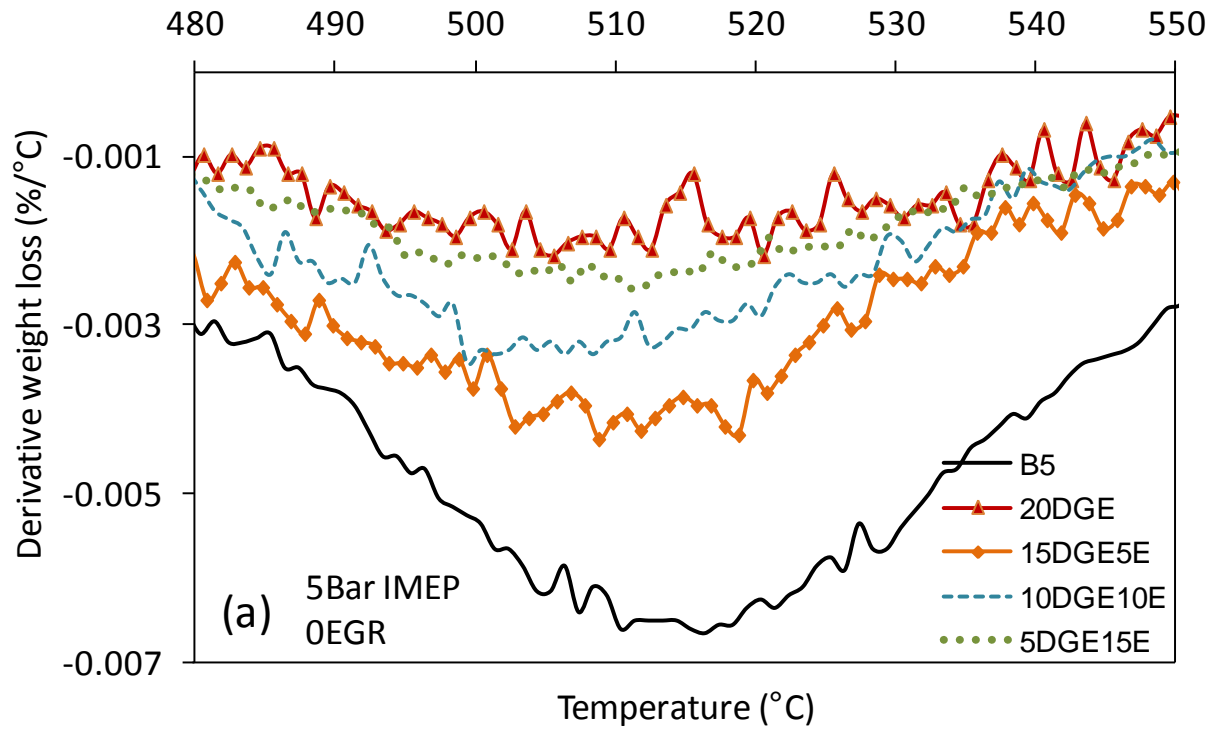


Figure 8