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1 **Reducing CO₂ footprint through synergies in Carbon Free Energy Vectors and Low Carbon**
2 **Fuels**

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7 **Abstract**

8 Carbon-footprint from transport and power generation can significantly be improved when
9 carbon free or reduced carbon energy carriers are utilised that are compatible with the current
10 technology of the internal combustion (IC) engines. The current study focuses on the reduction of
11 diesel engine CO₂ emissions by improving ammonia and hydrogen combustion through the
12 incorporation of alternative fuel, diethyl glycol diethyl ether (DGE) as an oxygenated fuel blend and
13 combustion enhancer. The aim of the work is to study the potential synergies between DGE and two
14 carbon free energy vectors H₂ and NH₃ in reducing the environmental effects and contribute in
15 decarbonising internal combustion engines. DGE's ignition properties (i.e. high cetane number)
16 improved the H₂ and NH₃ combustion efficiencies via counteracting their high auto-ignition
17 resistances, and also contributing in lowering the unburnt H₂ and NH₃ emissions to the atmosphere.
18 This led in the reduction of CO₂ by up 50% when 60-70% of diesel fuel is replaced with DGE, H₂ and
19 NH₃. Synergetic effects were also found between DGE and the gaseous fuels (i.e. hydrogen and
20 ammonia) simultaneously decreasing the levels of PM, NO_x, HC and CO emitted to the atmosphere;
21 thus mitigating the health and environmental hazards associated to diesel engines.

22 **Keywords:** DGE, hydrogen, ammonia, pollutants, emission control

23 **1. Introduction**

24 Current worldwide transportation relies primarily on fossil fuels. Effective decarbonisation of the
25 energy sector and especially transportation can be achieved by adopting fuel substitution with an
26 energy carrier free of carbon. Ammonia (NH₃) and hydrogen (H₂) can be renewably resourced by
27 utilising solar and wind energy. Hydrogen is believed to be one of the most potential alternatives [1]
28 but due to its low volumetric energy density and infrastructure challenges associated with its
29 transportation and handling, H₂ powered vehicles are still a niche product and widespread use is a

30 long term goal [2].

31 Ammonia has been studied as an energy [3] and hydrogen carrier for fuel cells [4, 5] and IC
32 engines, providing that there is a process to split the NH_3 into N_2 and H_2 [6]. In recent work we have
33 proposed that this is feasible through the application of the catalytic ammonia reforming and
34 decomposition using the heat of the engine exhaust gas to drive the reactions [2]. The combustion of
35 reformed gas, i.e. H_2 , N_2 , H_2O and unconverted NH_3 , in diesel engine with diesel fuels has shown to
36 reduce carbonaceous emissions, including CO_2 . However, under a range of engine operating
37 conditions, higher NO_x emissions and incomplete combustion of the reformed gas was seen, similarly
38 to LPG-diesel and natural gas-diesel dual fueled combustion, causing the production of other
39 undesired emissions such as NH_3 slippage [7]. Combustion improvements were observed in a study of
40 LPG-diesel and CNG-diesel fueled diesel engine with the use of a high cetane number fuel, such as
41 diethyl ether (DEE, CN >125) [8, 9]. Most recently, Ryu et al. [10] investigated the compression
42 ignition combustion of ammonia and dimethyl ether (DME, CN = 60), where several appropriate
43 strategies and fuel/gas mixtures were shown for the use of ammonia in direct-injection
44 compression-ignition engines. Apart from that, DME is also referred as a cetane enhancer blended
45 with different fuels/fuel mixtures for the purpose of particulate emission [11].

46 Similarly, diethyl glycol diethyl ether (DGE) can be regarded as another potential combustion
47 enhancer based on its high cetane (CN = 140) number and its high content of fuel-born oxygen.
48 Because of its featured high ignitability, DGE combustion in a diesel engine has a shorter ignition
49 delay and was demonstrated to burn sufficiently in low-temperature combustion regime under
50 charge-gas dilution and cooling [12]. All these characteristics of DGE can lead to the engine out
51 improved NO_x /soot trade-off when it combusted with diesel fuel. Also as being similar to DEE, its
52 presence (as fuel or fuel blend) in CI type of combustion is thought to be capable to assist the
53 combustion of those less ignitable fuel alternatives, such as H_2 and NH_3 .

54 In this work the impact of NH_3 and H_2 combustion on the CO_2 footprints of a diesel engine was
55 studied. Following that, the addition of reduced carbon fuel, named DGE at different amounts into
56 diesel, was studied as combustion improver of the carbon free gaseous fuels. The improvement in the
57 properties of the diesel fuel (i.e. cetane number, ignition properties and presence of oxygen content)
58 on the combustion and emission characteristics of the fuel mixture was assessed and compared in
59 order to identify potential CO_2 and other environmental benefits.

60 2. Experimental

61 *Test rig setup:* The NH₃ reformat was simulated using NH₃ and H₂ gas bottles, whose flows
62 were regulated by means of flow meters. The simulated gas additions were sent into the engine intake
63 and premixed with the intake air. The liquid fuel (pure diesel or DGE blend) was injected into the
64 cylinder to initiate the combustion. This approach required no modification to the fuel injection
65 system. A Thring Titan thyristor-type DC electric dynamometer was used to motor and load the
66 engine.

67 *Test engine:* The engine is a single-cylinder, direct injection, naturally aspirated diesel engine.
68 The main engine specifications are: bore 98.4 mm, stroke 101.6 mm, conrod length 165.0 mm,
69 displacement volume 773 cm³, compression ratio 15.5, maximum power 8.6 kW at 2500 rpm and
70 maximum torque 39.2 Nm at 1800 rpm.

71 *Data acquisition:* The data acquisition and combustion analysis were carried out using in-house
72 (University of Birmingham) developed Labview software. Output from the analysis of engine cycles
73 included the in-cylinder pressure and rate of heat release (ROHR) at varying crank angle degrees,
74 indicated mean effective pressure (IMEP), percentage coefficient of variation (COV) of IMEP values
75 and other combustion characteristics.

76 *Emission analysis:* The gaseous emissions including NO, NO₂, N₂O, CO, CO₂, THC (C₁ based)
77 and NH₃ were carried out by a MKS MultiGAS 2030 FTIR analyser (Fourier Transform Infrared
78 Spectroscopy). Detection limits are 3.6 ppm for NO, 1.2 ppm for CO and lower than 1 ppm for the
79 rest of gaseous species. Confidence intervals calculated using a 95% confidence level which reflects the
80 reliability and repeatability of the equipment are shown in the results. FTIR results have been verified
81 using known concentrations of CO₂, CO, NO, NH₃ and THC and a Horiba MEXA 7100DEGR (CO₂
82 and CO by Non-Dispersive Infrared, oxygen (O₂) by magnetopneumatic method, NO by
83 Chemiluminescence Detection and HC by Flame Ionisation Detector) gas analyser was used to
84 remove experimental bias during this procedure. Good agreement was obtained for the species and
85 emission levels shown in this investigation. The hydrogen concentration in the exhaust was measured
86 using a Hewlett Packard 5890 II gas chromatograph (GC) with thermal conductivity detector (TCD)
87 using argon as carrier gas. An investigation of particulate matter (PM) was carried out using a TSI
88 scanning mobility particle sizer (SMPS) 3080 electrostatic classifier to measure the particle size
89 distribution. The sample was thermo-diluted using a rotating disk, with the dilution ratio set to 200:1

90 at 150 °C. Particulate measurement is focus on small particulates (in the range from 10 to 400 nm)
91 being more dangerous for the environment and human health due to their higher reactivity, suspension
92 time in the atmosphere and alveolar deposition fraction (especially ultrafine particulates lower than
93 100 nm).

94 *Liquid fuel:* Ultra-low sulphur diesel (ULSD) fuel was used as the primary liquid fuel for
95 baseline operation. DGE was mixed volumetrically into the diesel to obtain the desired blends. Two
96 blends with volumetric concentrations of 20 and 40% of DGE (DGE20 and DGE40 accordingly) were
97 selected. This allowed a comparison between 3 different CN ratings and fuel-born oxygen contents.
98 The fuel properties are listed in Table 1 for each tested fuel/fuel blend.

99 *Test combinations of gaseous additions:* In a previous on-board ammonia dissociation study
100 using catalytic reforming technology [2], various amounts of hydrogen flow rates were produced
101 under different reactor conditions. Unconverted NH₃, N₂ and H₂O (no NO_x production) make up the
102 rest of the reactor product gas. For the purpose of current study, only H₂ and NH₃ were considered as
103 the effective (combustible) reforming products; the obtained volumetric H₂ to reformat (H₂ + NH₃)
104 ratio was ranging from 0.5 to 0.9, with roughly an increase of 0.1 from one reforming condition to
105 another. Hence to simulate the reformat gas at higher flow rate, the observed H₂/reformat ratio was
106 applied. The H₂ flows were chosen at 10, 15 and 20 l/min with various amounts of NH₃ selected
107 accordingly to meet the actual H₂/reformat ratios. Pure forms of H₂ and NH₃ were also adopted for
108 comparison purpose. All the H₂-NH₃ combinations are listed in Table 2.

109 *Test procedures:* The experimental runs were carried out in three separate sets for diesel and two
110 DGE blends i.e. DGE20 and DGE40. All tests were performed under steady – state conditions at a
111 controlled engine speed of 1500 rpm and a constant engine load of 5 bar IMEP throughout
112 representing about 65% of full engine load at this engine speed. In all test sets, the liquid fuel blend
113 was used to start and warm up the engine. Then different flows of NH₃ and H₂ or both combined were
114 added into the air intake. The amount of liquid fuel injection was modified accordingly after the
115 gaseous additions to keep the engine running at the same load. At least 20 minutes was allowed in
116 each run for stabilising the engine before any of the readings being taken.

117 **3. Results and discussion**

118 Liquid fuel replacement

119 The liquid fuel replacements on mass bases by the same quantity of gaseous fuels was higher in
120 the case of diesel fuel when compared to DGE-diesel blends as shown in Figure 1. As the DGE
121 content in the fuel blends was increased the amount of liquid fuel being replaced was reduced. This
122 was due to the lower LHV (i.e. higher fuel-born oxygen content, Table 1) of DGE than that of diesel
123 which increased the amount of DGE blend to keep the same engine load.

124 Combustion characteristics

125 The in-cylinder pressure and rate of heat release (ROHR) of diesel and diesel-DGE blends with
126 different gaseous additions are plotted in Figure 2a and b. While the addition of NH₃ (14 l/min)
127 prolonged the ignition delay in diesel combustion (Figure 2a), the DGE's high ignitability (see Table 1)
128 balances out the NH₃'s properties of high auto-ignition temperature (651°C) and octane rating (120) [10]
129 as can be observed by the advanced start of the combustion. It is suggested that the NH₃/air
130 pre-mixture being carried into the liquid fuel (diesel-DGE) spray periphery. When the liquid fuel
131 ignited, a flame was propagated to initiate the combustion of the mixture (premixed
132 DGE/diesel/NH₃/air) [9]. The beneficial effects of the oxygen content in DGE molecule could partially
133 compensate the effects of the reduction in the overall air/fuel ratio due to the oxygen dilution (decrease in
134 the intake air) from the incorporation of gaseous fuels at the air intake. By increasing the local
135 oxygen/fuel ratio the oxidation of the gas/fuel mixture was also facilitated. In addition, the DGE's
136 lower compressibility than diesel (usually inverse to density, see Table 1) could result in advanced
137 fuel injection and ignition that in turn benefits also the NH₃ ignition.

138 In the case of hydrogen addition, its high auto-ignition temperature and poor cetane rating did not
139 retard the start of combustion and that was the case in presence or not of ammonia (Figure 2). This is
140 due to the low ignition energy requirement for hydrogen (0.02 MJ/kg at stoichiometric H₂/air mixture)
141 being even lower than for many of the hydrocarbon components of the fuels [13, 14].

142 In terms of the ROHR patterns, the combustion of the diesel-NH₃ mixture intensified the
143 premixed phase and resulted in shorter combustion duration compared to diesel only combustion. This
144 was suggested to be due to the combustion of NH₃ and a high proportion of diesel in the premixed
145 combustion (because of the longer available time to mix air, NH₃ and the liquid diesel). On the other
146 hand, can be suggested that hydrogen's higher flame speed [15, 16] when compared to diesel and NH₃
147 led to faster and shorter combustion duration as can be seen by the larger increase in ROHR observed.
148 The addition of DGE in diesel reduced the premixed combustion phase for the two DGE-diesel fuel

149 blends. This was due to the DGE's much higher cetane number (140) compared to that of diesel (53.9).
150 As the DGE content increased, the ignition delay time was reduced and therefore suppressed the rate
151 of heat release in premixed combustion.

152 Compared to the diesel baseline, the presence of the combined NH_3 and H_2 also intensified
153 premixed combustion due to the rapid burning of H_2 which thermally favoured the ignition and
154 combustion velocity of NH_3 [17] and/or even decompose NH_3 into H_2 and N_2 [18]. These effects
155 contributed to the largely increased peak ROHR and hence the in-cylinder temperature (reflected by
156 the increased cylinder pressure) and shortened the overall combustion duration. The presence of DGE
157 in the combined NH_3 - H_2 combustion was again shown to reduce the intensity of the premixed
158 combustion and increase the total combustion duration with respect to the diesel- NH_3 - H_2 combustion.
159 The highest DGE concentration (i.e. DGE40) even further delayed the peak ROHR, which reduced
160 therefore the peak cylinder pressure, indicating the decreased combustion temperature. The total
161 combustion duration (combining the premixed and diffusion phases) and the ROHR in the diffusion
162 phase increase for both of the gases when applied with the DGE blends. These were based on their
163 diminished premixed phases, which indicate increased heat was released in the subsequent diffusion
164 phase compared to the combustion with diesel. And the overall increased heat release duration of
165 DGE than that of diesel in a broader range of in-cylinder conditions, enhances NH_3 and H_2
166 combustion.

167 The cyclic variation of the combustion was increased with NH_3 and H_2 addition, but the
168 coefficient of variation (COV) of IMEP was kept under 7% for all the conditions. The engine
169 instability could be derived from the increased incomplete combustion of these gaseous additions
170 from one cycle to another. This point will be further proved in the following section, using the unburnt
171 concentration of H_2 and NH_3 . The use of DGE improved the engine stability (COV of IMEP was
172 lower than 3 for all the tested conditions) by its combustion characteristics described earlier i.e. a)
173 reducing the cylinder pressure and hence the volatile in-cylinder condition through its low
174 temperature combustion and b) improving the combustions of H_2 and NH_3 via its higher ignitability
175 [19] and overall increased combustion duration.

176 CO₂ and unburned gaseous additions (NH_3 and H_2)

177 The trade-off between engine output CO_2 emissions and the volumetric NH_3 and H_2 emissions
178 under different fuelling conditions are shown in Figure 3a and b respectively. The ammonia measured

179 in the engine exhaust was reduced significantly by the addition of H₂. This was in accordance with the
180 H₂ improved NH₃ combustion shown in Figure 2b. However, the unburned NH₃ and H₂ emissions are
181 still high and other reasons such as NH₃ and H₂ escaping the combustion process during the process of
182 charge exchange should be also considered.

183 *NH₃ and H₂:* As it is shown in Figure 3a and b, the presence of DGE also improved the emissions
184 of NH₃ and H₂ for all the studied cases (diesel-NH₃, diesel-H₂ and diesel-H₂-NH₃ combustion). This is
185 especially noticeable when higher additions of ammonia and hydrogen are used. DGE20 slightly
186 improved unburnt NH₃ emissions compared to diesel fuelling while the improvement was even further
187 under the presence of hydrogen (Figure 3a). This is due to the beneficial effect of DGE20 on
188 hydrogen combustion (Figure 3b) which also enhances NH₃ combustion (synergetic effect) reducing
189 the unburnt H₂ and NH₃ emissions. Further incorporation of DGE (DGE40) does not statistic
190 significantly improve further hydrogen combustion, but reduces unburnt NH₃ emissions.

191 The ignition properties of DGE enhanced the combustion pattern (see Figure 2), which improved
192 also the ammonia and hydrogen combustion and hence reduced the unburnt ammonia and hydrogen
193 due to, for example, the flame quenching on the chamber walls and the ammonia-air mixture trapped
194 within the piston-ring crevice. The largest emissions of hydrogen and ammonia were recorded when
195 DGE was absent and with a co-feeding of NH₃ and H₂ at 14 and 15 l/min. The combined gaseous
196 addition replaced 29 l/min of the air intake flow, which represented 6% of air reduction in the overall
197 intake charge. This brought the same dilution effect reducing the in-cylinder oxygen concentration
198 (similarly to exhaust-gas-recirculation, EGR), which could result in incomplete combustion [20].
199 Furthermore the increased fuel replacement by high gaseous additions (Figure 1) also affects the
200 diesel spray characteristics, which were thought to restrict the source of ignition for the gaseous
201 additions. On the other hand, the low heating value of the DGE blends with respect to diesel results in
202 a longer injection duration in addition to the longer combustion duration which increase the available
203 time of the liquid fuel spray and diffusion combustion in the combustion chamber to ignite the
204 gaseous fuels. Therefore, the fuel-born oxygen brought by DGE and DGE's high ignitability were
205 inferred to alleviate the i) intake air shortage, ii) poor auto-ignition properties of the gaseous fuels and
206 iii) reduction of the liquid fuel spray assisting the mixture's ignition and combustion.

207 *CO₂ emissions:* When NH₃ is combusted the CO₂ emissions released to the atmosphere are
208 significant reduced due to the absence of carbon in the NH₃ molecule, but high unburnt NH₃ was

209 released to the atmosphere resulting in a CO₂-NH₃ trade off (Figure 3a). The incorporation of H₂ to
210 diesel-NH₃ combustion enables to simultaneously decrease further the engine output CO₂ and NH₃
211 emissions. However, for high H₂ and NH₃ intake concentrations there is some unburnt hydrogen
212 which is not efficiently combusted (Figure 3b). The use of DGE-diesel blend decreased the
213 tank-to-wheel (TTW) CO₂ emissions due to the high O/C ratio compared to diesel combustion. The
214 incorporation of DGE into the liquid diesel fuels enhances the combustion of the carbon free gaseous
215 fuels (H₂ and NH₃) and simultaneously decreases the engine output levels of CO₂, NH₃ and H₂
216 released to the atmosphere. The reduction of CO₂ reached approximately 50% of the initial CO₂
217 emission recorded from the combustion of diesel fuel only.

218 From the results presented above, it is suggested the large decrease in engine output NH₃
219 emissions could be due to a number of phenomena, where the DGE could first enhance the individual
220 combustions of H₂ and NH₃, and more importantly, the improved H₂ combustion and its fast flame
221 speed and propagation subsequently favouring the NH₃'s combustion, resulting in a synergetic effect
222 between the gaseous and liquid fuels overall improving the combustion process. This sequenced
223 pattern is displayed in Figure 4.

224 Brake thermal efficiency

225 The brake thermal efficiencies (BTE) of the engine at different H₂-NH₃ additions were calculated
226 using Eq. 1 and are shown in Figure 5.

$$227 \quad \eta = \frac{P_{\text{Brake}}}{(\text{LHV} \times M_f)} \quad \text{Eq. 1}$$

228 Where P_{Brake} is the engine brake power, M_f is the fuel mass flow rate and LHV is the lower
229 heating value of each fuel and gas (i.e. Diesel, DGE, NH₃ and H₂).

230 In general, the addition of H₂ and NH₃ into diesel operation decreased the engine thermal
231 efficiency. This is associated with less efficient combustion of H₂ and NH₃ as described earlier with
232 reference to Figure 3. Although the NH₃'s combustion was enhanced by the presence of H₂, it was not
233 to the same extent as that of the baseline diesel. For a simple comparison, the hydrocarbon emission
234 (C₁ based) at the 100% diesel baseline never exceeded 450 ppm at the studied load operation. In
235 addition, part of the decrease could be also related to the intake air replacement by the H₂ and/or NH₃
236 that reduced the overall volumetric efficiency. Apart from the above, H₂ was reported to decrease the
237 thermal efficiency in diesel combustion due to its higher flame velocity and small quenching distance

238 [21, 22] that increased heat loss to the chamber walls.

239 The DGE addition (DGE40, as an example) was shown to increase the BTE due to the improved
240 H₂ and NH₃ utilisation as can be proved by the reduced emissions of H₂ and NH₃ under the DGE
241 addition.

242 Other gaseous emissions

243 *CO and THCs:* Similar trends to CO₂ are also observed for the emission reductions of CO and
244 unburnt hydrocarbons (Figure 6a and 6b, respectively). The locally enriched fuel-born oxygen
245 enhanced the complete fuel combustion, suppressing the formation of CO and THC [23]. In addition,
246 the replacement of carbon based fuels, the more advanced ignition and overall prolonged combustion
247 duration with the DGE blends (Figure 2b), increased the available time for CO and THC oxidation.
248 The combustion properties of DGE are believed to support its easier (high CN rating) oxidation even
249 in the late combustion stage, helping in removing the CO and THC that escaped from the main
250 combustion events.

251 *NO_x Emissions:* The PM-NO_x emissions (NO + NO₂) trade-off of the diesel and DGE blends
252 with and without NH₃ and H₂ additions are plotted in Figure 7. Without hydrogen, the NO_x emission
253 is shown to increase at small NH₃ additions (up to 3 l/min). When larger quantities of ammonia were
254 added, the effects of (i) low combustion flame temperature of NH₃ [24] (ii) delayed start of
255 combustion and consecutively retarded combustion, (iii) lower oxygen availability, all combined
256 leading in suppressing NO_x production. As shown in the same plot, when the highest NH₃ flow (14
257 l/min) was used, the NO_x emissions became even lower than that of the diesel baseline.

258 On the other hand, the improved NH₃ combustion with hydrogen inevitably enhanced the NO and
259 NO₂ emission from that of the diesel baseline and is shown to be proportional to the hydrogen level
260 (Figure 7). Although DGE was demonstrated to improve the NH₃'s combustion, further decrease in
261 NO_x was observed due to the increased DGE presence (with and without the hydrogen addition). As
262 indicated earlier in the combustion profile (Figure 2), the addition of DGE reduced the cylinder
263 pressure (i.e. combustion temperature), especially in the premixed combustion phase where the NO_x
264 formation is most significant. As a result, NO_x formation was further suppressed even the hydrogen
265 promotion effect on NH₃ combustion for the DGE40 blend.

266 On the other hand, N₂O emissions with the combined fuelling of H₂, NH₃ to liquid fuel combustion
267 (for both diesel and DGE blends) were higher than those of just liquid fuel combustion. Around 10-15%

268 of the N₂O was reduced after the DGE blends being applied. This result needs to be further
269 investigated in order to control N₂O emissions due to its high global warming potential.

270 Particulate matter emissions

271 The particulate size distribution and mass concentrations at different levels of DGE, H₂ and NH₃
272 are shown in Figure 8a-c and d-f respectively. The total PM emissions expressed in g/kWh are plotted
273 in the NO_x-PM trade-off (Figure 7). The particle mass distribution was obtained from the particle
274 number distribution through a size dependent agglomerate density function as described by Lapuerta
275 et al. [25]. It has to be noted that only particulates in the range of 10 to 400 nm have been considered
276 for the total PM estimation. In the case of larger particulates are included the PM emissions would be
277 higher.

278 Combustion of the DGE blends showed simultaneous reductions in NO_x and PM emissions with
279 and without gaseous additions, especially when 40% (v/v) of DGE is incorporated to the diesel fuel
280 blend. The primary reason was again the oxygen present in the DGE molecule. This would allow
281 enhanced combustion to take place even in the fuel rich area, which helped to oxidise the PM that
282 were already formed or improve the oxidation of particles and particle precursors [26-28]. In addition
283 to that, the prolonged combustion duration (Figure 2) at increased DGE level also provided longer
284 time for the PM oxidation. Another reason for this PM reduction was based on the fact that DGE is in
285 the form of ether [11, 29]. Due to its atomic structure of being one oxygen atom bound to two carbon
286 atoms, the DGE structure was reported to effectively inhibit soot formation, which counts for a large
287 portion in total PM.

288 After adding hydrogen and ammonia, the mass and number of PM were reduced for both diesel
289 and DGE blends due to the large replacement of carbon through decreasing the formation of local fuel
290 rich regions. The individual performance of H₂ and NH₃ are shown to improve at increased DGE level.
291 This is supported by the reduced H₂ and NH₃ emissions shown earlier, meaning enhanced carbon
292 replacement were achieved by better H₂ and NH₃ combustion. It is seen that H₂ alone performed better
293 in PM reduction than that of NH₃. This is in accordance with the more pronounced premixed phase in
294 H₂ combustion. The PM emission reduced when simultaneous additions of NH₃ and H₂ were adopted
295 and decreased further with use of DGE. The number and mass particulate matter size distributions
296 were decreased across the size spectrum (Figure 8), and hence decreased total mass emissions as
297 shown in Figure 7. These trends further support the above proposed DGE combustion enhancement

298 (Figure 4), which in turn improved also the PM and NO_x reduction.

299 **4. Conclusions**

300 Carbon free energy carriers and low carbon renewable fuels such as ammonia and hydrogen can
301 be used in existing power generation technologies but there are challenges that need to be answered
302 from the production to storage (especially on-board) and efficiency utilisation. In this research, the
303 extent of the environmental benefits (i.e. CO₂ and other pollutants) that can be achieved when
304 synergies in the utilisation of carbon free energy vectors (NH₃ and H₂) and reduced carbon renewable
305 fuels such as DGE are identified and assessed. These results are obtained for a research single
306 cylinder engine. It is believed that quantitative results will depend on engine technology, but general
307 trends and fundamental understanding of the roles of hydrogen and DGE on NH₃ combustion gained
308 by this research are also applicable to modern multi-cylinder engines for practical applications. It has
309 to be noted that the further potential to improve thermal efficiency and CO₂ emissions due to the
310 possibility of using part of waste exhaust energy in the endothermic reforming process has not been
311 considered. In addition, only the effects of the carbon-free fuels NH₃ and H₂ have been studied here,
312 while the effects on combustion and emissions of N₂ produced by ammonia dissociation process have
313 not been investigated as those effects have been already studied in the literature.

314 The study demonstrates that low carbon renewable fuels such as DGE, can directly impact in
315 CO₂ emissions but most importantly can be designed to have the suitable properties to enhance the
316 utilisation of carbon free energy carriers, in this case ammonia and hydrogen. By easing the utilisation
317 of new environmentally friendly fuels and energy carriers, both CO₂ levels emitted to the atmosphere
318 (up to 50% demonstrated here on tank-to-wheel bases) as well as other harmful pollutants can be
319 depleted. The synergies between DGE and carbon-free gaseous fuels have also led in the reduction of
320 other emissions (i.e. CO and hydrocarbons) and shifted the well-known diesel engine PM and NO_x
321 trade-off to lower values. In addition, the combination DGE's molecule oxygen content and good
322 ignition properties allowed counteracting for the replacement of oxygen part of the air with the
323 induction of gaseous fuel.

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Table captions

Table 1: Fuel properties of the tested liquid fuel/blend.

Table 2: H₂ and NH₃ additions to the engine intake.

Table 1

	ULSD	DGE	DGE20	DGE40
Chemical Formula	$C_{14}H_{26.18}$	$C_8H_{18}O_3$	$C_{12.52}H_{24.16}O_{0.74}$	$C_{11.20}H_{22.36}O_{1.40}$
Molar Mass (kg/kmol)	194.18	162	186.24	179.16
Density at 15 °C (kg/m³)*	827.1	908	843.3	859.46
LHV (MJ/kg)**	42.99	31.4	40.49	38.10
Cetane Number	53.9	140	-	-
C (wt%)	86.52	59.2	80.67	75.02
H (wt%)	13.48	11.1	12.97	12.48
O (wt%)	0	29.7	6.36	12.50

* Estimated based on volumetric fraction

** Estimated based on mass fraction

Table 2

H₂ (l/min)	20.0				15.0				10.0				0.0			
NH₃ (l/min)	0.0	3.0	7.5	14.0	0.0	3.0	7.5	14.0	0.0	1.0	7.5	14	1.0	3.0	7.5	14.0
H₂/Reformate	1.0	0.9	0.7	0.6	1.0	0.8	0.7	0.5	1.0	0.9	0.6	0.4	0	0	0	0

Figure captions

Figure 1: Liquid fuel replacement by different H₂ and NH₃ additions.

Figure 2: In-cylinder pressure and ROHR of the combustions of diesel and DGE blends with (a) separate additions of NH₃ and H₂ and (b) simultaneous addition of NH₃ and H₂, the flow rates for NH₃ and H₂ are 14 and 15 l/min respectively.

Figure 3: CO₂ and unburned gaseous additions trade-off for (a) NH₃ and (b) H₂ at different fuelling conditions.

Figure 4 Combustion pattern proposed for DGE enhanced NH₃ and H₂ combustion.

Figure 5: Engine brake thermal efficiencies of the combustions of standard diesel and DGE blend with different combinations of H₂ and NH₃.

Figure 6: Carbonaceous gaseous emissions of diesel and DGE blends with different combined additions of H₂ and NH₃ (a) CO and (b) THC.

Figure 7: NO_x-PM trade off.

Figure 8: PM number distributions for PM (a) diesel, (b) DGE20 and (c) DGE40 and PM mass distributions for (d) diesel, (e) DGE20 and (f) DGE40

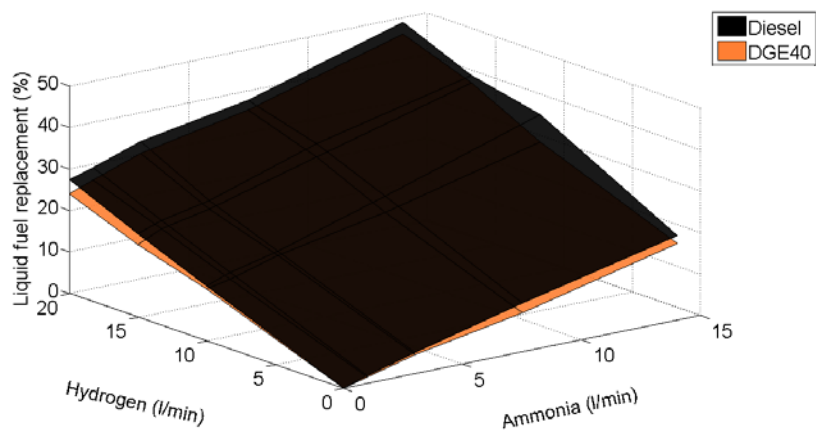


Figure 1

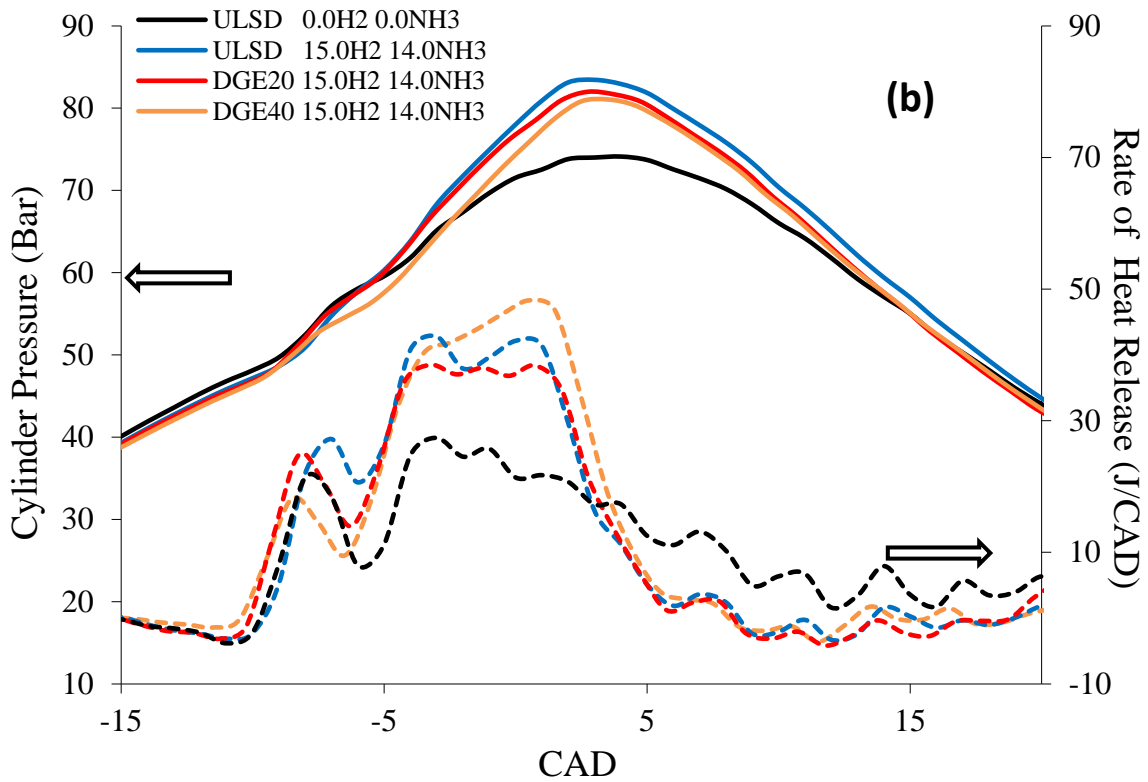
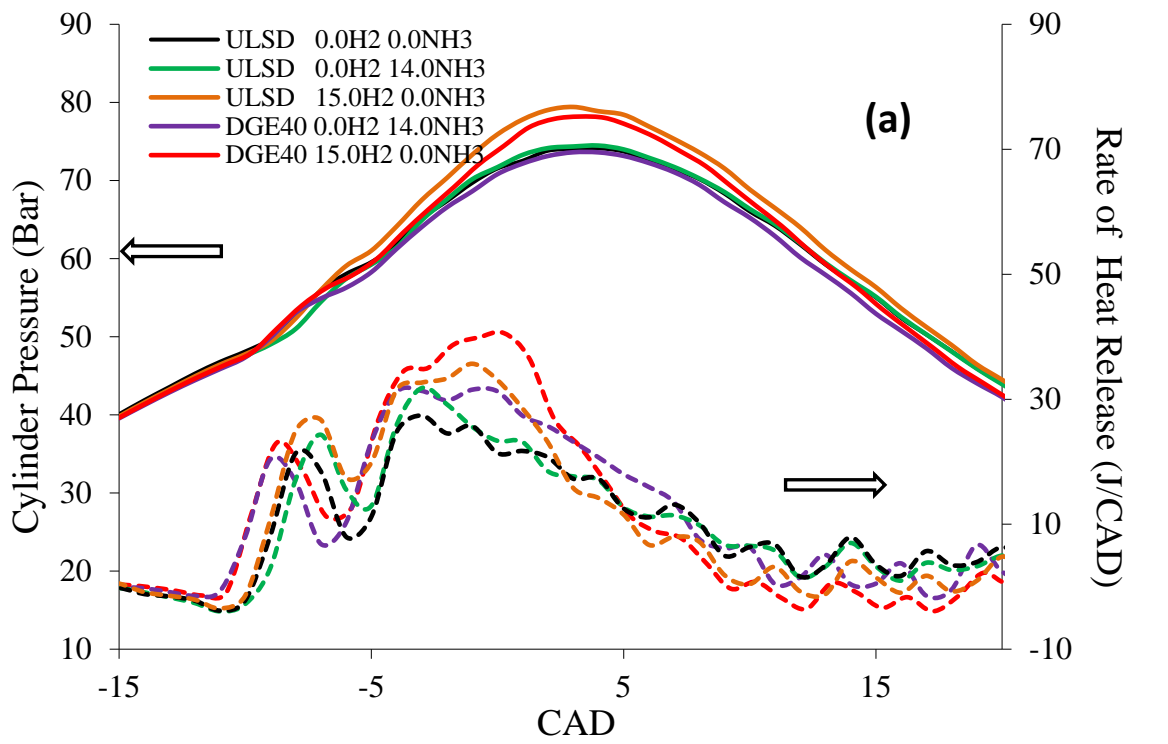


Figure 2

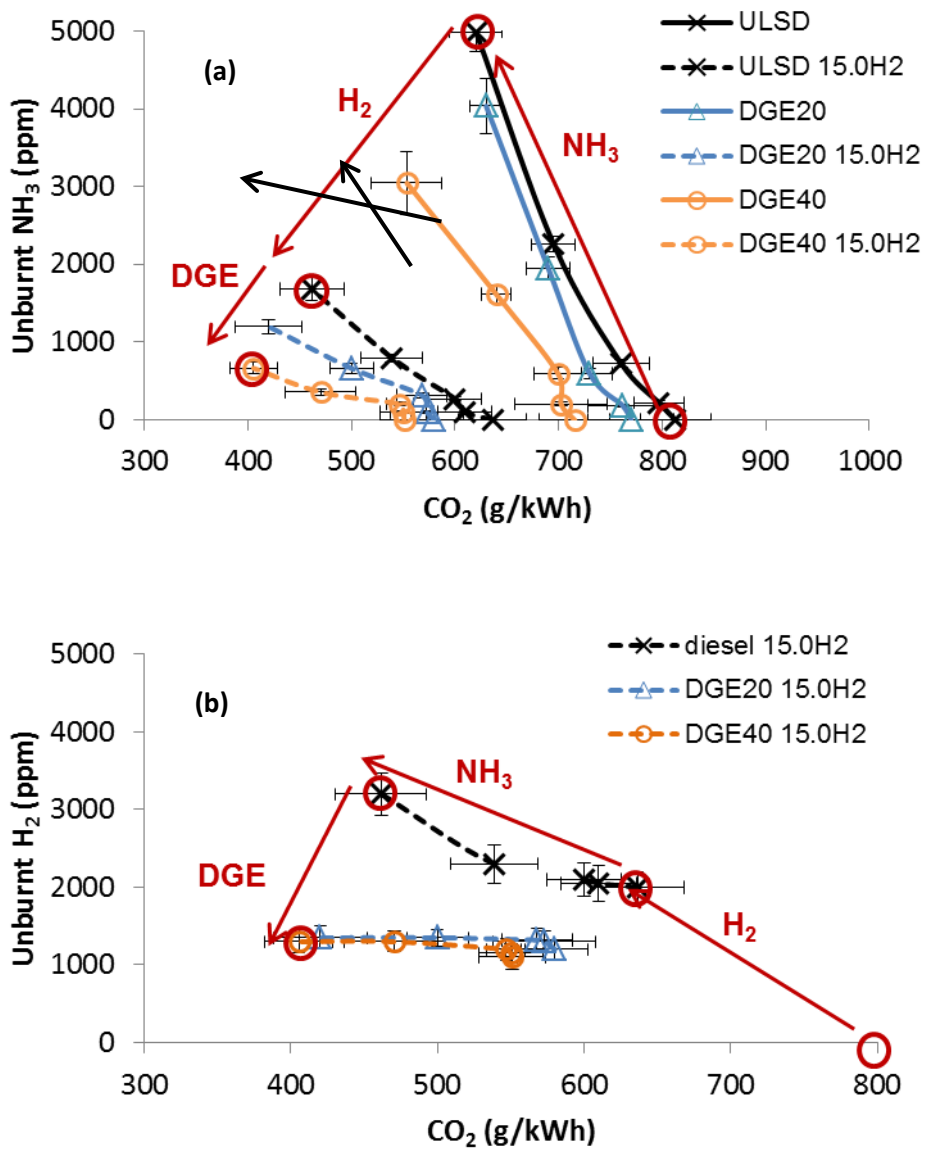


Figure 3

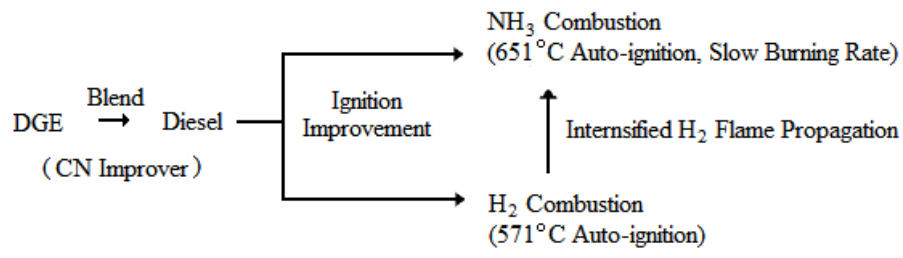


Figure 4

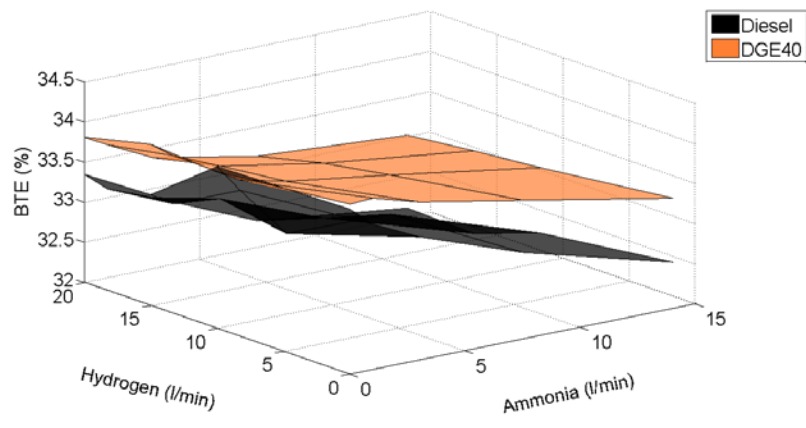


Figure 5

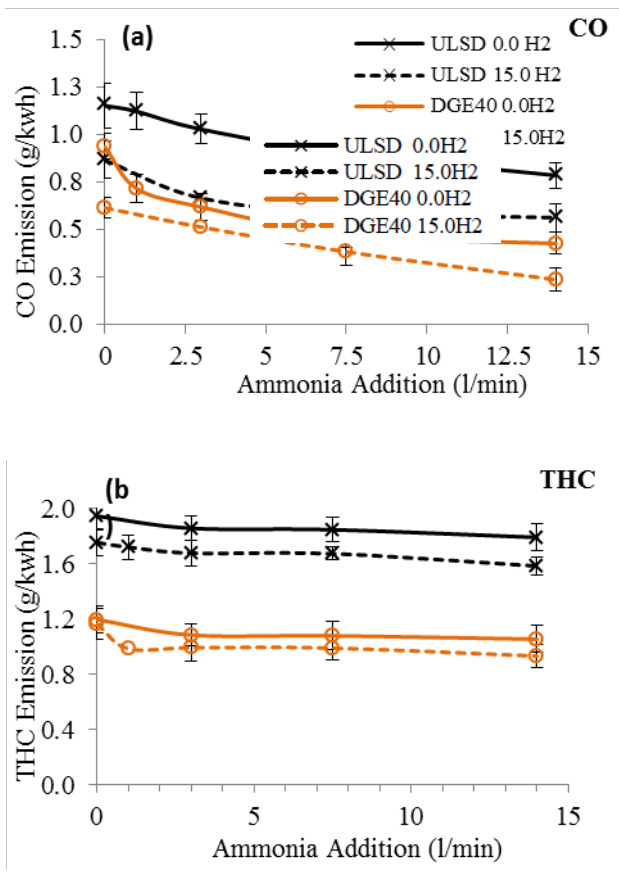


Figure 6

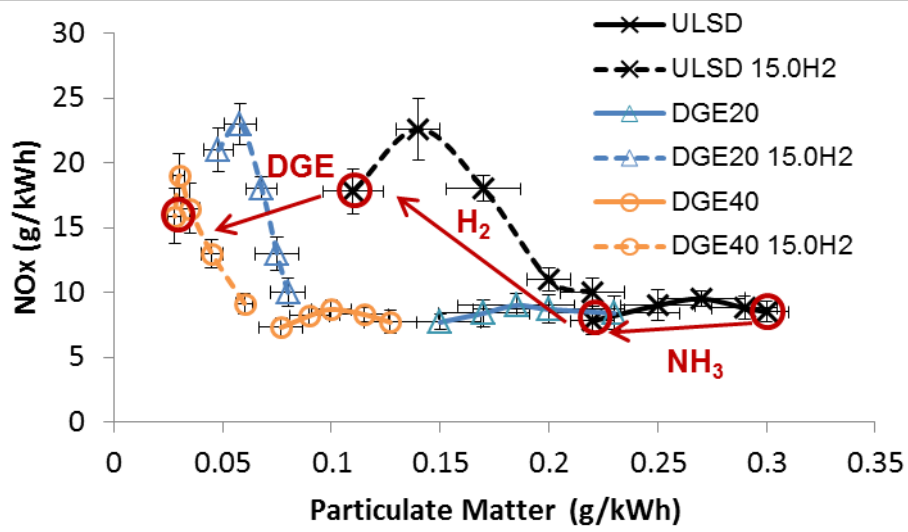


Figure 7

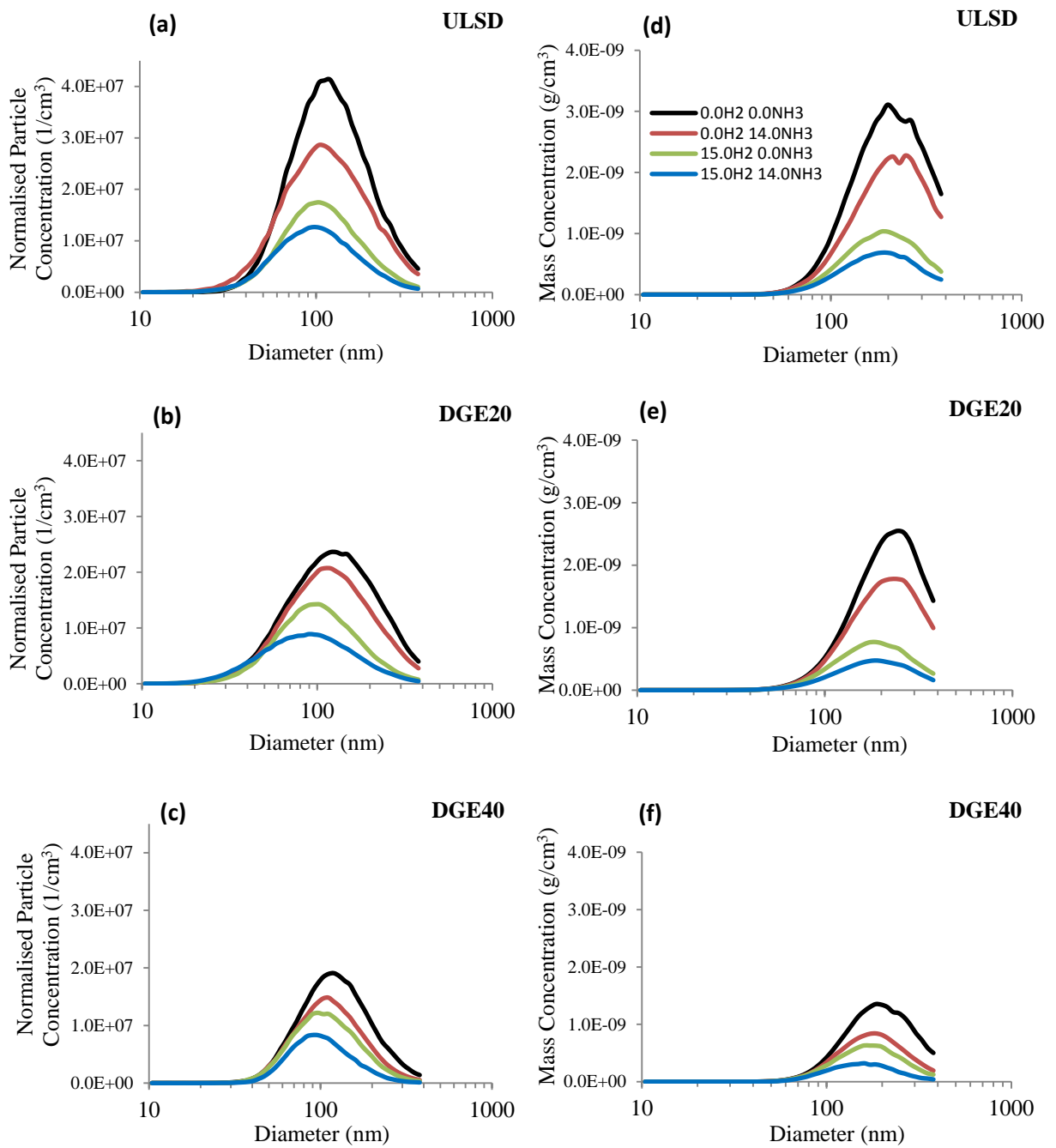


Figure 8