

# Manipulating modern diesel engine particulate emission characteristics through butanol fuel blending and fuel injection strategies for efficient diesel oxidation catalysts

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1 **Manipulating modern diesel engine particulate emission characteristics through butanol fuel**  
2 **blending and fuel injection strategies for efficient diesel oxidation catalysts**

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11 **Abstract**

12 Decoupling the dependences between emission reduction technologies and engine fuel economy in  
13 order to improve them both simultaneously has been proven a major challenge for the vehicle research  
14 communities. Additionally, the lower exhaust gas temperatures associated with the modern and future  
15 generation internal combustion engines are challenging the performance of road transport  
16 environmental catalysts. Studying how fuel properties and fuel injection strategies affect the  
17 combustion characteristics, emissions formation and hence catalysts performance can unveil synergies  
18 that can benefit vehicle emissions and fuel economy and as well as guide the design of next generation  
19 sustainable fuels. The experimental work presented here was conducted using a modern single-  
20 cylinder, common rail fuel injection system diesel engine equipped with a diesel oxidation catalyst  
21 (DOC). The impact of the fuel post-injection strategy that is commonly used as part of the  
22 aftertreatment system function (i.e. regeneration of diesel particulate filters or activity in hydrocarbon  
23 selective reduction of NO<sub>x</sub>), combined with butanol-diesel fuel blend (B20) combustion on engine  
24 emissions formation, particulate matter characteristics (size distribution, morphology and structure)  
25 and oxidation catalyst activity were studied. It was found that post-injection produced lower PM  
26 concentration and modified the soot morphological parameters by reducing the number of primary  
27 particles ( $n_{po}$ ), the radius of gyration ( $R_g$ ), and the fractal dimension ( $D_f$ ). The results were compared  
28 with the engine operation on diesel fuel. The increased concentration of HC and CO in the exhaust as  
29 a result of the diesel fuel post-injection at the studied exhaust conditions (i.e. T= 300 °C) led in the  
30 reduction of the DOC activity due to the increased competition of species for active sites. This effect  
31 was improved the combustion of B20 when compared to diesel.

32 **Keywords:** alternative fuels, diesel oxidation catalyst, gaseous emissions, particulate matter, post-  
33 injection, butanol

## 34 1. Introduction

35 With the view to improve the air quality, new engine and vehicle systems and technologies are  
36 under development in order to reduce pollutants emitted to the atmosphere especially in the very  
37 challenging transportation sector [1, 2]. In road transport, replacing fossil fuels with biofuels also  
38 provide cleaner combustion and consequently improve the efficiency of the catalytic aftertreatment  
39 systems and can be considered as a way to help vehicle manufacturers to achieve the emissions  
40 legislative limits such as the EURO 6 and CARB (LEV III) [3].

41 Bioalcohols and other oxygenated fuels have been reported to reduce emissions, when  
42 replacing gasoline fuels in spark-ignition (SI) engines. More recently these fuels have been studied as  
43 substitute to diesel fuel [4-8] because of their oxygen content that contributes in the reduction of the  
44 engine out CO, UHC (unburned hydrocarbons), NO<sub>x</sub> (nitrogen oxides) and total PM emissions. It is  
45 reported that the hydroxyl group present in alcohols is more efficient in reducing diesel engine PM  
46 than other functional groups with the same oxygen content, especially at high engine loads [9-11]. The  
47 combustion of diesel-ethanol blends for example has been widely reported to reduce PM emissions [4,  
48 12]. However, there are also drawbacks [13, 14] such as the ethanol's limited solubility in diesel fuel  
49 [15], the very low cetane number and the lower dynamic viscosity, parameters that can impact on the  
50 engine's operation and combustion characteristics [4, 16, 17]. Butanol in diesel has shown more  
51 promising characteristics as an alternative fuel to ethanol [4] due to higher cetane number and better  
52 solubility in diesel fuel as a consequence of being less polar than other alcohols with shorter chain.  
53 Furthermore, it has higher heating value, lower volatility, and less hydrophilic character [18, 19].

54 Modern engine after-treatment systems consist of different components such as the diesel  
55 oxidation catalysts (DOC) and diesel particulate filters (DPF) [20]. DOCs have a honeycomb monolith  
56 shape with high cell density (large surface area) and suitable loadings of a catalytic material such as  
57 platinum and/or palladium that is able to almost eliminate CO, HC and much of the particulate organic  
58 fraction [16, 20, 21]. DOC also oxidise NO to produce NO<sub>2</sub> that can then be utilised in the DPF to  
59 passively oxidise soot at low temperatures [16, 22, 23]. The DOC's activity depends on exhaust gas  
60 temperature, residence time of the exhaust gas in the catalyst, level and nature of gaseous and  
61 particulate matter exhaust species and inhibitions/synergies between the different species contained in  
62 the exhaust gas [23, 24]. In the same way, DPF performance is also influenced by size and morphology  
63 [fractal dimension ( $D_f$ ), radius of gyration ( $R_g$ ) and number of primary particles ( $n_{po}$ )] of soot particles  
64 making understand their control challenging [16, 25]. Therefore, the effect of fuel and engine operating  
65 parameters such as injection settings (e.g. number of injections, injection timing, injection pressure,  
66 injection quantity) needs to be understood in order to improve not only the engine performance  
67 (power/torque) characteristics but also the function of the aftertreatment system [26]. Several studies

68 have shown that the post-injection in combination with the DOC is commonly used to increase the  
69 exhaust gas temperature in order to aid the DPF regeneration (i.e. active regeneration) [27].

70 The impact of fuel post-injection on engine out gaseous emissions and PM has also been  
71 investigated [28-30]. The temperature increase late in the combustion cycle due to the post-fuel injection,  
72 which can enhance soot oxidation, produced during the main combustion event [30-34], but this is reported  
73 to be dependent on the engine calibration and operation conditions. Some studies have reported PM  
74 increase with post-injection at high engine loads and speeds [28]. In some cases post-injection also  
75 contributes in the reduction of engine out NO<sub>x</sub> due to the formation of nitrated-hydrocarbons through  
76 the reactions of NO<sub>x</sub> with HC radicals [35, 36]. It is reported that CO and THC are reduced with post-  
77 injection and sharply increased with later post-injection timing (after 70 CAD ATDC) [27]. Late  
78 combustion caused by post-injection increases the level of THC emissions as the late injected fuel is  
79 not burnt in the combustion chamber [26, 29, 37]. In this way, HCs are oxidized in the DOC, increasing  
80 considerably the temperature of the exhaust upstream of the DPF and trapping a high proportion of  
81 the soot flowing in the exhaust stream [27, 38, 39]. It is documented that the main-post-injection  
82 increases the rate of soot oxidation in the combustion cycle due to the enhancement of the gas mean  
83 temperature and air/fuel mixing, which leads to the reduction in number and diameter of primary  
84 particles [40, 41].

85 Combined advances in alternative fuels and aftertreatment systems are required in order to  
86 fulfil the stringent emission regulations and also help in decoupling mutual dependences between  
87 pollutants control and engine fuel economy. Most of the studies on alternative fuels combustion  
88 published in the literature are focused on the effect of the fuel on the engine performance and on the  
89 engine emissions, including PM characteristics [17] which influences passive and active DPF  
90 regeneration [20] as well as DPF trapping efficiency [42, 43]. Recent studies have reported work on  
91 gaseous emissions interactions [22] and the influence of PM characteristics [16] (size and shape)  
92 emitted from the combustion of different fuels on the DOC performance. However, there is still scarce  
93 information regarding the effect of alternative fuels (e.g. alcohol blends) on both, PM characteristics  
94 and DOC activity with simultaneous use of fuel post-injection, strategy that is required in diesel  
95 vehicles for catalyst heat-up in active and DPF regeneration. Therefore, the aim of this research work  
96 focuses on the role of the fuel post-injection and diesel-butanol fuel blends combustion on PM  
97 characteristics (number, size, morphology) and the impact on the DOC activity. The DOC catalyst  
98 activity was assessed under the same temperature, space velocity and pressure conditions with the only  
99 comparative parameter being the exhaust gas composition.

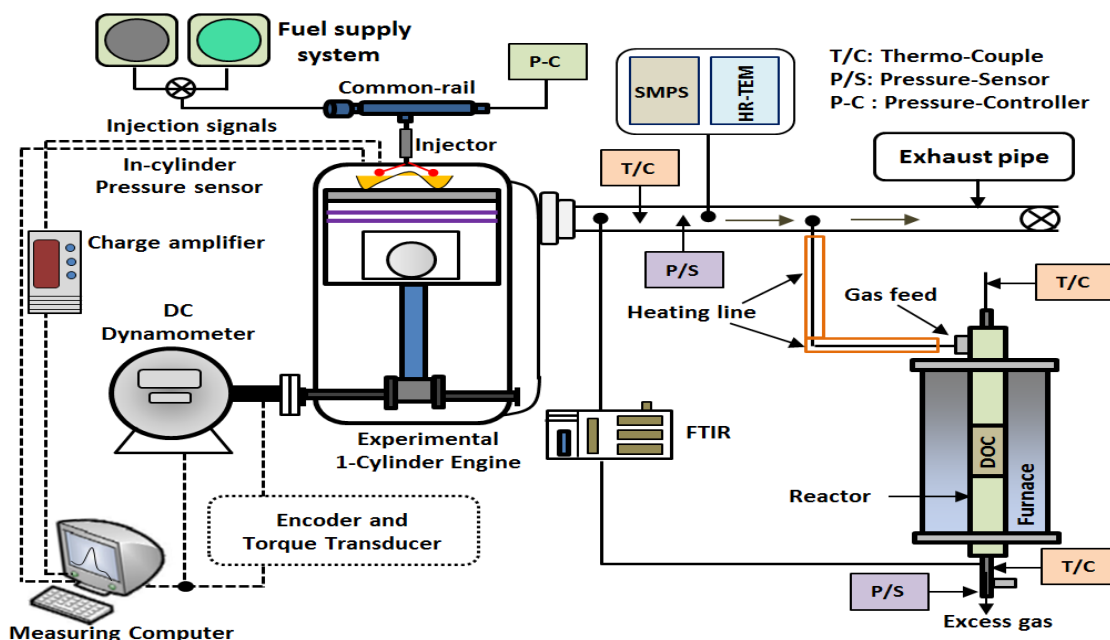
100 **2. Experimental setup and materials**

101 A modern single-cylinder, water-cooled, common rail fuel injection system, four-stroke  
 102 experimental diesel engine was employed in this investigation. The engine used in this study is a single  
 103 cylinder research engine that was designed by the investigators and incorporates one of the cylinder  
 104 heads of a V6 production engine. The main specifications of the test engine can be found in Table 1.  
 105 A schematic diagram of the experimental set up is shown in Figure 1. The diesel oxidation catalyst  
 106 studies were carried out using one inch in diameter monolith catalyst that was placed in a reactor inside  
 107 a furnace where the temperature and the engine exhaust gas flow can be controlled by a thermocouple  
 108 (located upstream the catalyst) and a flow meter respectively.

109 **Table 1.** Research engine specifications.

Engine parameters	Specifications
Engine type	Diesel 1- Cylinder
Stroke Type	Four-Stroke
Cylinder Bore x Stroke (mm)	84 x 90
Connecting Rod Length (mm)	160
Compression Ratio	16.1
Displacement (cc)	499
Engine Speed Range (rpm)	900 – 2000
IMEP Range (bar)	< 7
Fuel Pressure Range (bar)	500 – 1500
Number of Injections	3 injection events

110



112 **Figure 1.** Schematic diagram of test platform and sampling system.

113 The Ultra Low Sulphur Diesel (ULSD) fuel used for the study was supplied by Shell Global  
 114 Solutions UK. Butanol was purchased from Fisher Scientific Company and used in this study for the

115 diesel-butanol blends. The ULSD, butanol and fuel blend properties are presented in Table 2. The  
 116 particular diesel fuel used in this research as reference fuel was selected without any biodiesel (thereby  
 117 with zero oxygen content) in its composition, in order to study the effect of the oxygen in the  
 118 combustion process when diesel fuel is blended with butanol. The diesel-butanol blend (B20) is a mix  
 119 of 80% diesel and 20% butanol (%Vol.).

120 **Table 2.** Fuels specification [4, 16].

Properties	Method	ULSD	Butanol	B20D80
Cetane number	ASTM D7668-14	50.2	17	41.98
Latent heat of vaporization (kJ/kg)		243	585	-
Bulk modulus (MPa)		1410	1500	-
Density at 15 °C (kg/m <sup>3</sup> )	EN 12185	840.4	809.5	833.2
Upper heating value (MJ/kg)		45.76	36.11	43.5
Lower heating value (MJ/kg)		43.11	33.12	40.91
Water content by coulometric KF (mg/kg)	EN 12937	40	170	389.4
Kinematic viscosity at 40 °C (cSt)	EN ISO 3104	2.564	2.23	2.27
Lower Calorific Value (MJ/kg)		43.11	33.12	39.95
Lubricity at 60 °C(μm)	EN ISO 12156	424	571.15	444.5
Fatty acid methyl ester % (v/v)	NF EN 14078-A	<0.05		
Cold filter plugging point (CFPP)	ASTM D-6371	-18	<-51	-18
C (wt %)		86.44	64.78	81.56
H (wt %)		13.56	13.63	13.35
O (wt %)		0	21.59	4.318

121 At significantly lower or higher than 300 °C exhaust gas temperatures; the impact of fuels and  
 122 post injection strategy on the DOC may not be as robust and conclusive as the catalyst may not light-  
 123 off (low load) or the activity may not be affected (high loads). All tests were performed under a  
 124 constant engine speed of 1800 rpm with an engine load of 3 bar IMEP (Indicated Mean Effective  
 125 Pressure). An AVL GH13P was used to record the in-cylinder pressure [44]. The charge from the  
 126 pressure transducer (mounted in the cylinder head) was amplified by an AVL FlexiFEM 2P2 Amplifier  
 127 [45]. A digital shaft encoder producing 360 pulses per revolution was used to measure the crank shaft  
 128 position. The data from the crank shaft position and pressure was combined to create an in-cylinder  
 129 pressure trace. The engine is equipped with common-rail fuel injection system which allows the  
 130 control of multiple injection events. The injection was split in pre, main, and post fuel injection with  
 131 injection timing of 15 and 3 deg bTDC and 60 deg aTDC, injection pressure of 650 bar, and post-  
 132 injection duration of 0.1 ms. A bespoke experimental facility was used in this study that was designed  
 133 to assess the performance of catalysts and combination of aftertreatment systems under real engine  
 134 exhaust gas while providing flexibility with temperatures and reductants (i.e. hydrocarbons, ammonia,  
 135 hydrogen) selection. The DOC used in this study was supplied by Johnson Matthey Plc and was  
 136 positioned inside a mini reactor that was located inside a furnace and was fed with real engine exhaust

137 gas. The temperature upstream the DOC was monitored using K-type thermocouples. The temperature  
138 of the reactor inside a tubular furnace was set at 300 °C while maintaining constant gas hourly space  
139 velocity (GHSV) of 35000 h<sup>-1</sup>. The details of the catalyst (DOC) used in this study was a 4.237 kg/m<sup>3</sup>  
140 with optimal platinum:palladium proportion (weight ratio 1:1) with alumina and zeolite washcoat  
141 (158.66 kg/m<sup>3</sup> loading). The total dimensions of the DOC were 25.4 mm diameter, 91.4 mm length,  
142 and 4.3 mil wall thickness of the DOC [16, 22, 23].

143 A MultiGas 2030 FTIR spectrometry based analyzer was employed for exhaust gaseous  
144 emissions measurement such as: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen oxide (NO  
145 and NO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), and individual hydrocarbons species such as methane (CH<sub>4</sub>), ethane  
146 (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>). Particulate Size Distributions (PSD) were analysed using a TSI 3080  
147 scanning mobility particle sizer (SMPS). Exhaust gas part was sampled and diluted with air when  
148 using the rotating disk thermodiluter (TSI 379020A) to control the dilution ratio. The dilution ratio  
149 was set at 1:100 for all the tests and the thermodiluter temperature was 150 °C. The SMPS was  
150 connected downstream of the dilution system in order to extract a diluted sample for the particle size  
151 measurement.

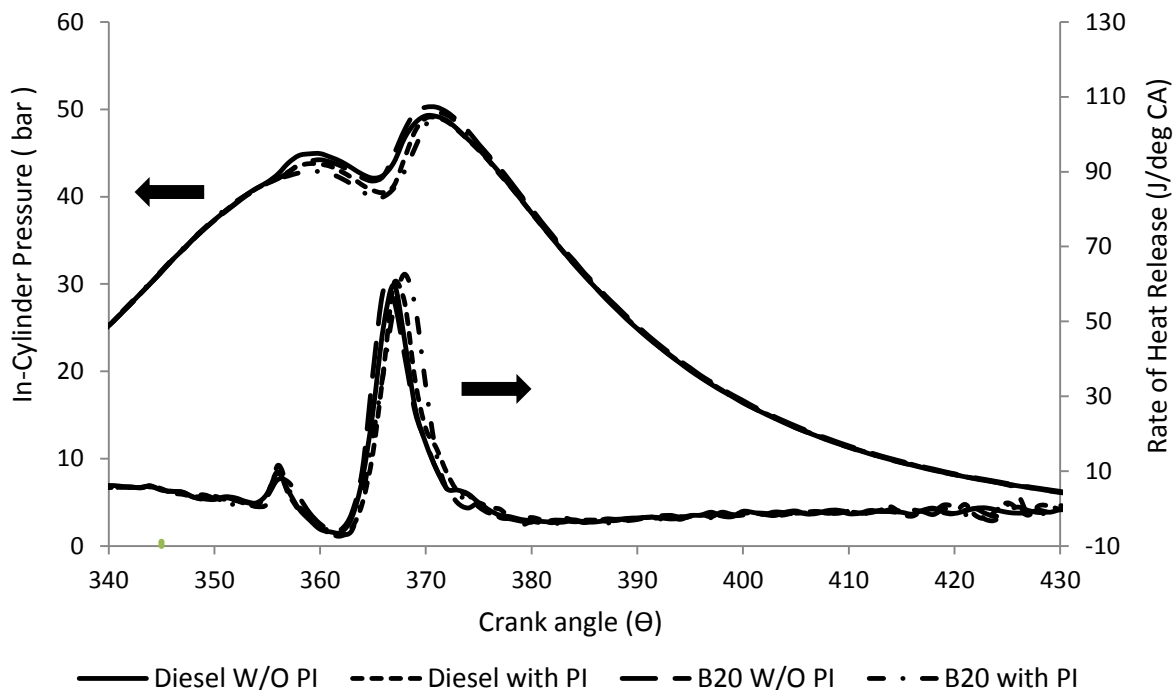
152 Soot particles were collected from the exhaust pipe on a 3.05 mm diameter copper grids  
153 attached to a sampling probe. The sampling tool and lines were cleaned with nitrogen before each test  
154 to remove deposited soot particles. A Philips CM-200 high resolution transmission electron  
155 microscopy (HR-TEM) with a resolution about 2 Å at an accelerating voltage of 200 kV was used to  
156 analyse the particles. A digital image analysis software in Matlab was designed to calculate the  
157 morphological parameters of the agglomerates (radius of gyration, R<sub>g</sub>, number of primary particles,  
158 n<sub>po</sub>, and fractal dimension, D<sub>f</sub>) [46, 47]. The conversion from pixels to nanometres was calibrated by  
159 comparison with standard latex spheres shadowed with gold. For each condition, two grids and  
160 minimum 33 photographs were taken per fuel to calculate the morphology parameters as well as least  
161 26 agglomerates were chosen for each condition and fuel to obtain the results. Furthermore, more than  
162 200 primary particles were manually and randomly selected from different aggregates to determine an  
163 average diameter of primary particles and to produce the fitted normal distribution of primary particles  
164 at each fuel and condition.

### 165 **3. Results and discussions**

#### 166 **3.1 Combustion characteristics**

167 Figure 2 shows the effects of the injection strategy on the in-cylinder pressure and the rate of  
168 heat release (ROHR) versus crank angle degree (CAD) for the combustion of diesel and B20. It has to  
169 be noted that neither the post-injection nor the fuel properties notably affected the combustion events.  
170 It is though that this is due to the effect of the pre-injection which thermally conditioned the in-

171 cylinder, thus minimizing the effect of the worse autoignition properties (Table 2) of the B20 blend  
 172 with respect to diesel fuel. Small increase of the in-cylinder pressure and heat release was obtained  
 173 from the combustion of B20 that may also explain the changes in emissions later on.

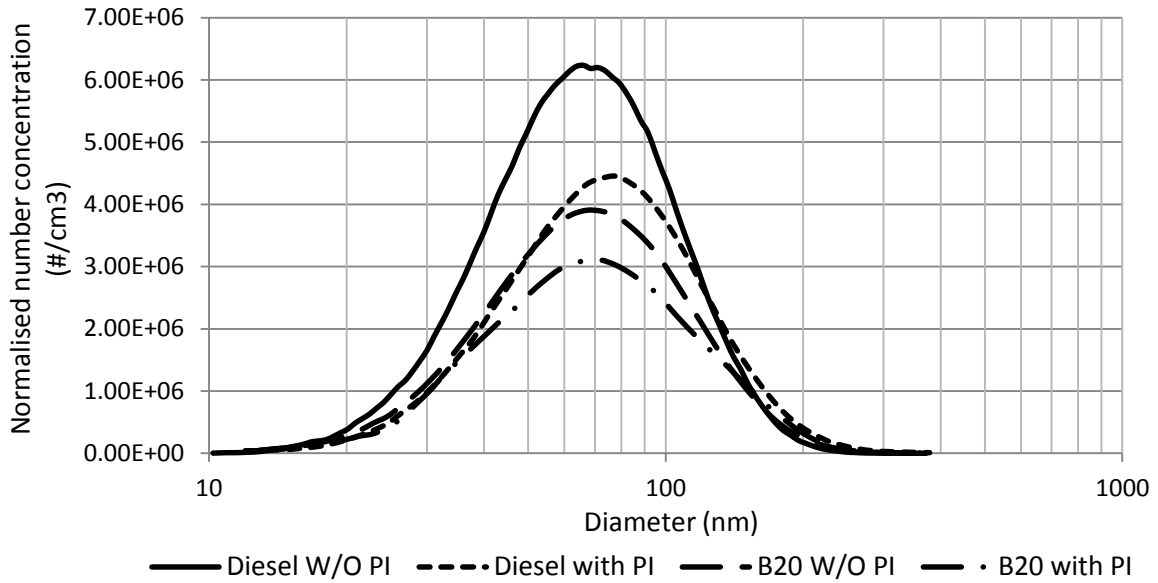


175 **Figure 2.** Effect of fuel post-injection strategy and fuels structure on combustion characteristics.

176 **3.2 Influence of fuel post-injection and fuel structure on engine out PM and gaseous emissions**

177 The PSDs were obtained upstream the DOC in order to understand the influence of B20 and  
 178 post-injection on the particle formation and oxidation processes. The combustion of the alcohol blend  
 179 (B20) reduced the number of particles along the whole distribution with respect to combustion of the  
 180 diesel fuel with and without post-injection (Figure 3). A slight reduction is observed in the average  
 181 particle diameter, from 94 nm for diesel down to 64 nm for B20 in the absence of post-injection. These  
 182 results are in agreement with previous studies of butanol-diesel blends combustion [16, 48] justified  
 183 by the presence of the hydroxyl group in the butanol molecule [16] leading to lower rates of PM  
 184 formation [4, 16] and to enhanced PM oxidation rates [16, 49]. Reductions of the soot in the exhaust  
 185 are often reported when post-injection is introduced due to increased expansion temperature and  
 186 enhanced mixing within the cylinder that increases oxidation of soot produced from the main injection  
 187 [30, 32-34].





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189 **Figure 3.** Effect of post-injection on particle size distribution for diesel and B20 fuels.

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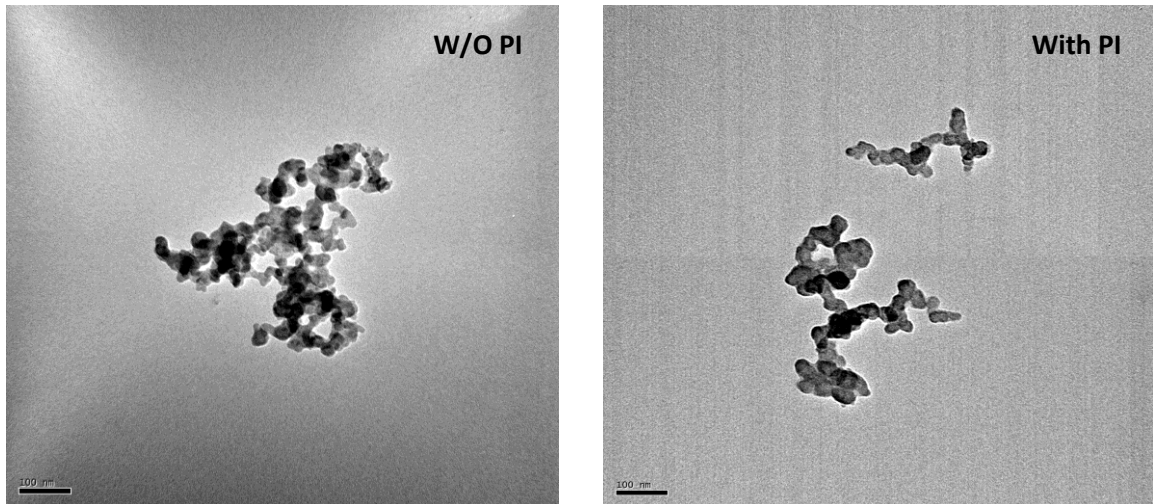
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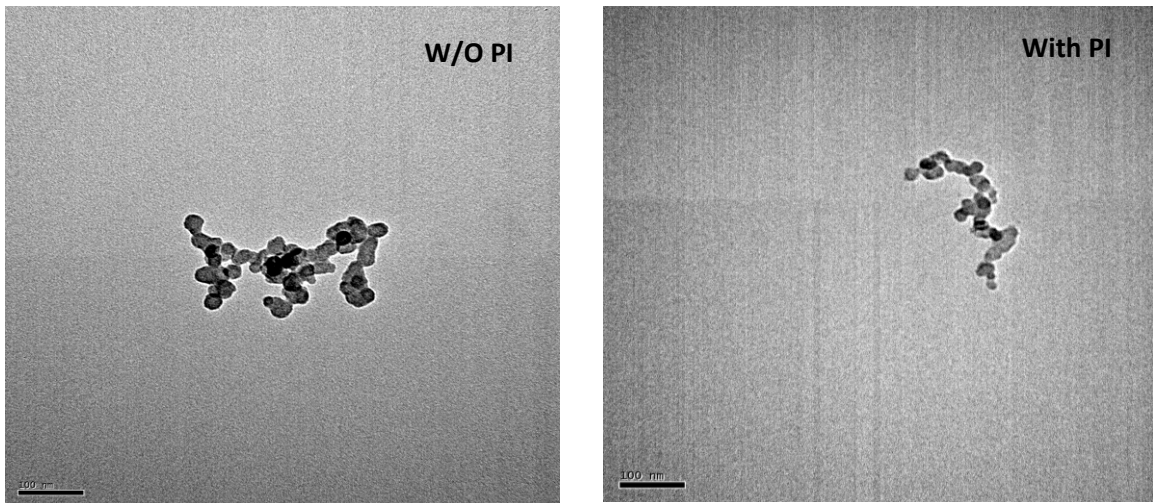
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The particles emitted from diesel engine have a variety of shapes and sizes and consist of tens to hundreds of primary particles agglomerated together, forming irregular clusters [50, 51]. Figure 4 depicts representative examples of HR-TEM micrographs from particles sampled from the exhaust gas at the different conditions studied in this research. PM morphological parameters (radius of gyration ( $R_g$ ), number of primary particles ( $n_{po}$ ) and fractal dimension ( $D_f$ )) for Diesel and B20 are calculated from the obtained HR-TEM images. Figure 5 shows the results of the average particles electrical mobility diameter obtained with SMPS jointly with soot's average radius of gyration and number of primary particles. According to these results the average agglomerate size (quantified by radius of gyration and mobility diameter) and the number of primary particles are lower for B20 than for diesel fuel independently of the injection strategy. It is believed that for diesel combustion the enhanced net formation rate of particles increases the likelihood of collisions and further aggregation leading to higher number of primary particles. It is thought that oxygen content in butanol blend (B20) improves the soot oxidation [52] while the incorporation of the post-injection leads to enhanced oxidation resulting in the disappearance of a fraction of the primary particles already formed (Figure 5). The reduction in number of particles as measured by the SMPS and the reduction in number of primary particles in the particle aggregate for B20 are also associated with the reduction in the formation of soot precursors due to the chemical structure of butanol and the lack of PAH in butanol, besides the effect of the oxygen content of butanol.

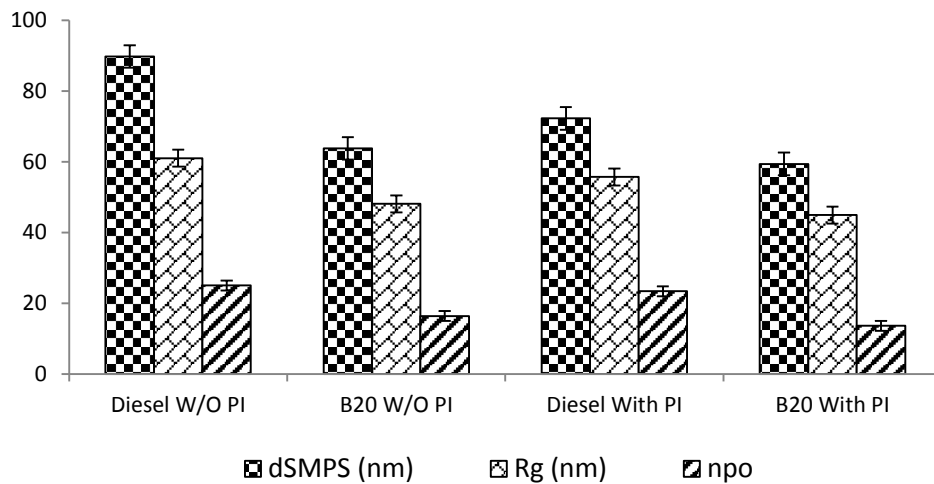


(a)



(b)

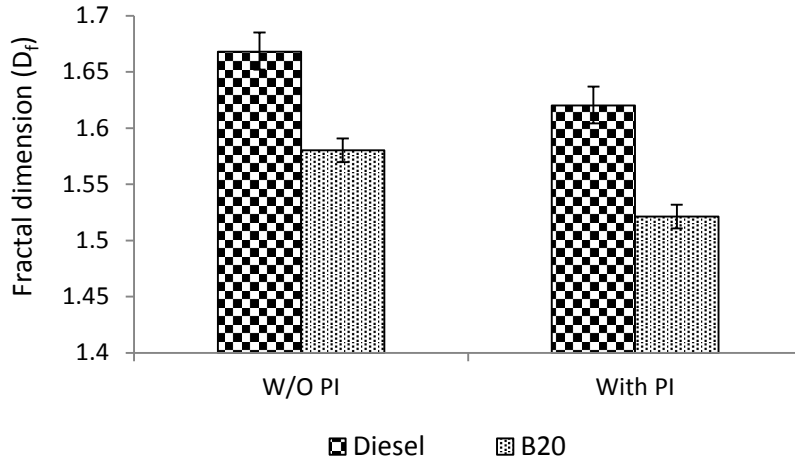
208 **Figure 4.** Typical examples of HR-TEM micrograph of particles matter collected at the exhaust gas  
 209 for (a) diesel fuel, and (b) B20.



210

211 **Figure 5.** Effect of fuel injection strategy and fuel characteristics on particle size from SMPS, radius  
 212 of gyration ( $R_g$ ) and number of primary particles ( $n_{po}$ ).

213           The influence of the fuel and injection strategy (with and without post-injection) on the fractal  
214 dimension ( $D_f$ ) is shown in Figure 6. The fractal dimension of the agglomerates produced from the  
215 diesel fuel is higher (by 1.62-1.66) than that from B20 for both injection strategies (Figure 6) and this  
216 is in agreement with the work described by both Fayad et al. [16] and Choi et al. [53]. As a general  
217 rule a reduction of the fractal dimension should be expected when there is a high concentration of  
218 particles as a result of the increased likelihood of collisions between agglomerates. However, in the  
219 case of agglomerates from oxygenated fuels, despite the lower particle concentration (and the  
220 consequent reduced likelihood of collisions) fractal dimensions were not found to be higher, but were  
221 systematically lower instead, probably due to some internal oxidation of agglomerates occurring after  
222 being formed. Similarly, the fractal dimension is also lower when post-injection was introduced for  
223 both fuels, despite the higher particle concentration also in this case (Figure 6). A conceptual model is  
224 suggested here to justify these trends. In the early stage of nuclei and primary particle formation fractal  
225 dimension is close to 3 and the primary particle size continuously increases (spherical nuclei and  
226 spherical primary particles). Collisions between particles and agglomerates and between agglomerates  
227 and agglomerates will increase the size of the agglomerate and reduce their fractal dimension (particle  
228 growth dominant over particle oxidation). This phenomenon will be more intense in the case of diesel  
229 without post injection conditions due to the higher rate of particle formation. Afterwards, the oxidation  
230 of particles will become dominant over the particle formation and the size of both primary particles  
231 and agglomerates could decrease, while the fractal dimension will deeply decrease, for the reason  
232 pointed out above. In this case, the decrease in fractal dimension will be more intense for the case of  
233 oxygenated fuels and post-injection conditions. Therefore, it is speculated that the resultant  
234 agglomerates from oxygenate fuels and post-injection conditions will have lower fractal dimension as  
235 the oxidation will remain being the dominant mechanism in front of particle formation and growth for  
236 longer time, as a consequence of the enhanced reactivity of soot particles (in the case of oxygenated  
237 fuels/) or of the enhanced temperature conditions in the exhaust flow (in the case of post-injection).  
238 More research and some in-cylinder sampling techniques should be used for a more comprehensive  
239 justification.



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241 **Figure 6.** Fractal dimensions of particulate matter from the HR-TEM images.

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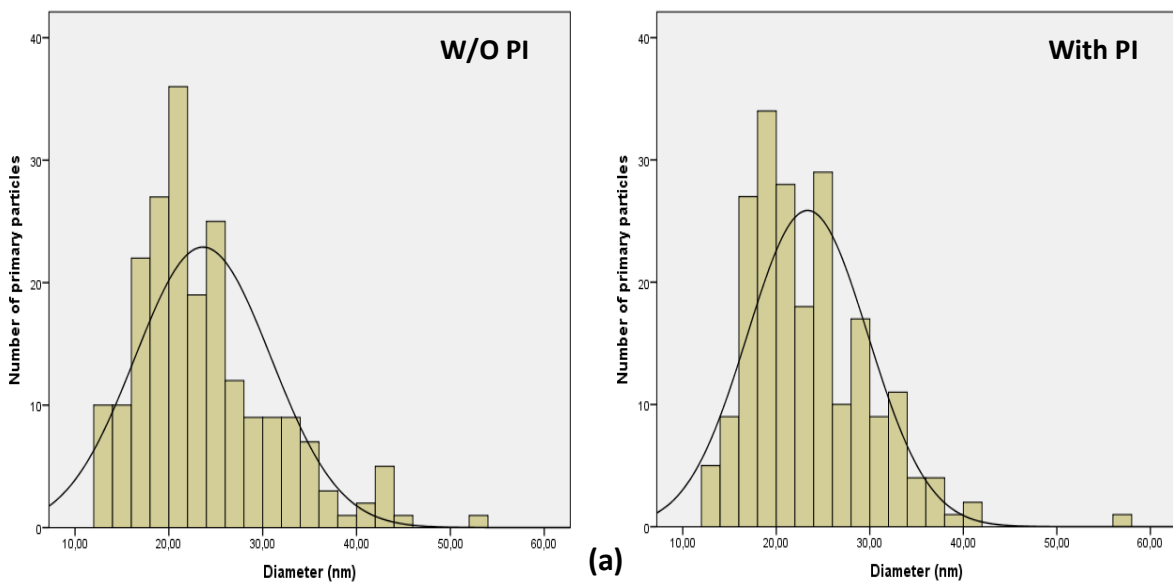
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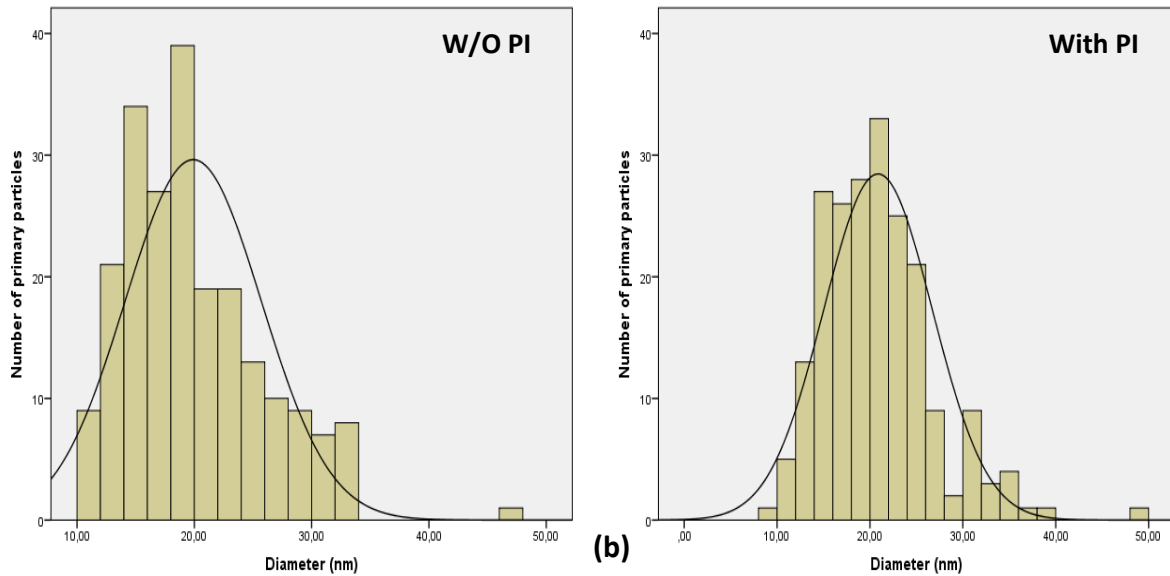
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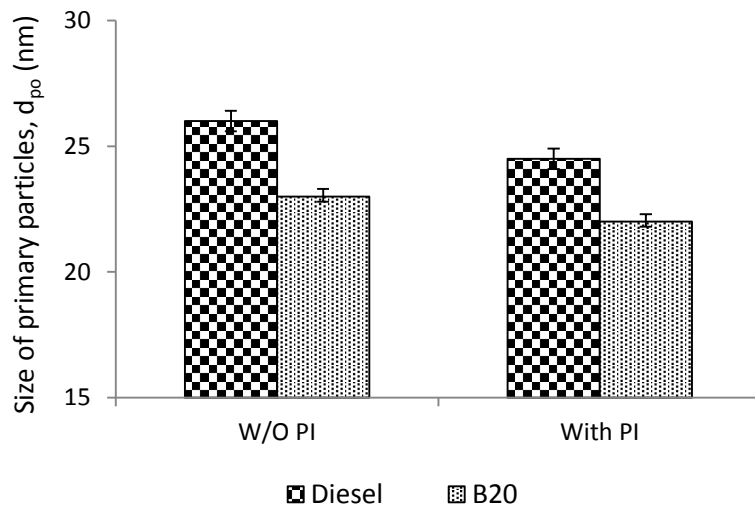
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The primary particle diameter ( $d_{p0}$ ) size distribution for both fuels with or without post-injection has been measured by selecting around 200 primary particles (more than 33 HR-TEM photographs for each condition and fuel) in order to fit normal distribution as shown in Figure 7. Figure 8 shows smaller size primary particles from the combustion of B20 for both injection setting (with and without post-injection) compared to diesel primary particles due to lower rate of production of soot precursors, soot formation and soot growth, and to the increase soot oxidation during the combustion of oxygenated fuel [16]. This result is in agreement with results obtained from biodiesel fuel [54] and butanol [16, 55] fuel blends without post-injection using other engine technologies [16, 55]. The size of primary particles is slightly reduced when post-injection was used for both fuels (Figure 8). It is believed this is due to an enhancement in the soot oxidation rate in the expansion stroke under post-injection conditions.





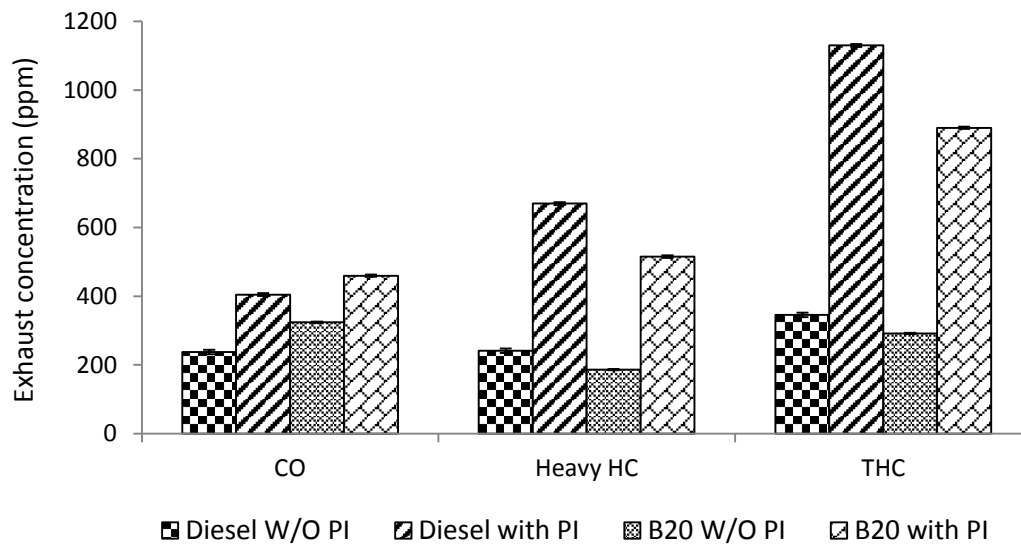
253 **Figure 7.** Primary particles size distributions for (a) diesel fuel, and (b) B20.



254  
255 **Figure 8.** Average size of primary particles ( $d_{po}$ ) for diesel and B20.

256 Figure 9 shows the CO, heavy HC, and THC engine-out emissions for the two studied fuels at  
 257 both injection strategies. It can be noticed that THC emissions were lower from the combustion of the  
 258 alcohol blend (B20) for both injection strategies. The higher HC emissions observed with diesel can  
 259 be attributed to several reasons including absence of oxygen in the fuel molecule, and less efficient  
 260 oxidation. The THC emissions in the case of post-injection are much higher compared to the case  
 261 without post-injection. This confirms that the quantity and timing chosen for the post-injection allows  
 262 to keep most of them unburnt and available to be oxidised in the DOC. Yamamoto, et al. and Chen,  
 263 [26, 30] reported that the late post-injection lead to high level of THC emissions. It is reported that the  
 264 reason of the increase in CO emissions observed for B20, especially without post-injection, can be

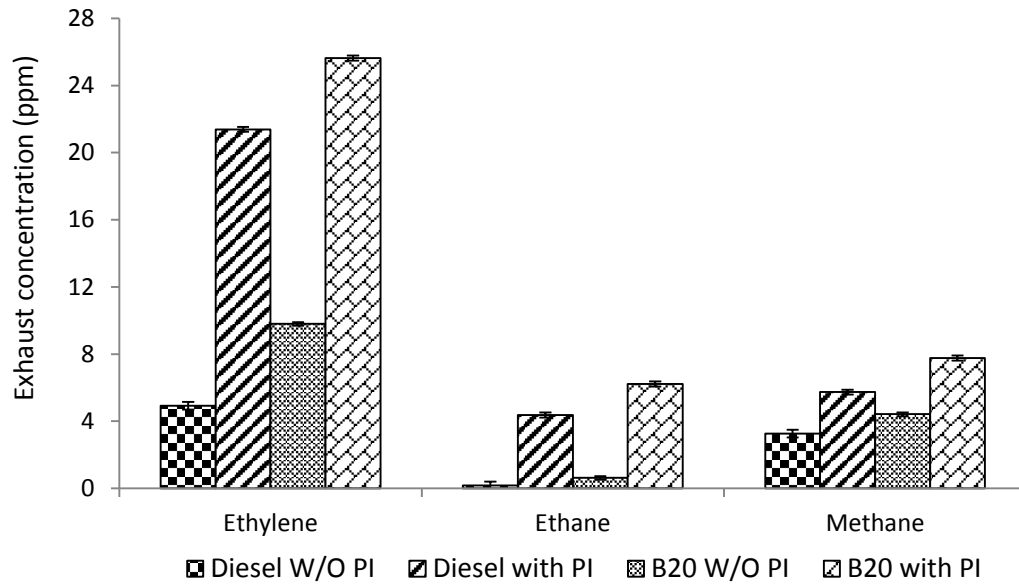
265 attributed to the expected lower local in-cylinder temperature (Figure 2) and less CO oxidation during  
 266 the combustion process due to the higher enthalpy of vaporisation of butanol with respect to diesel  
 267 fuel [27]. Therefore, it seems that at this engine load operation the oxygen content and high reactivity  
 268 of the butanol molecule enables to partially oxidise most of the HC species to CO, but the colder in-  
 269 cylinder conditions due to the enthalpy of vaporization of butanol hinders the complete oxidation from  
 270 CO to CO<sub>2</sub>.



271

272 **Figure 9.** Engine exhaust gaseous emissions.

273 The concentration of HC species in the engine exhaust upstream the catalyst differs for diesel  
 274 and B20 engine fuelling (Figure 10). The concentration of the light HC species studied including  
 275 saturated (methane, ethane) and unsaturated (ethylene) species is higher for B20 with respect to diesel  
 276 fuel combustion, conversely to the THC emissions presented earlier. It is thought that this is due to the  
 277 thermal decomposition of the butanol component to light HC species and CO rather than forming  
 278 heavy HC components as in the case of diesel fuel combustion. The level of HC emissions was lower  
 279 from the combustion of B20 compared to the diesel fuel combustion. This can be due to improved  
 280 combustion efficiency of the fuel in the presence of oxygen in the fuel as has also been described in  
 281 [56] and due to the combustion patterns described in Figure 2, where a small increase in the in-cylinder  
 282 pressure was obtained. From the results it can be also observed that with the incorporation of the fuel  
 283 post-injection, higher concentration of the total and selected HC species were measured for both fuels  
 284 due to the late timing of the post-injection [26].



285

286 **Figure 10.** Engine exhaust hydrocarbon species measured upstream the DOC.

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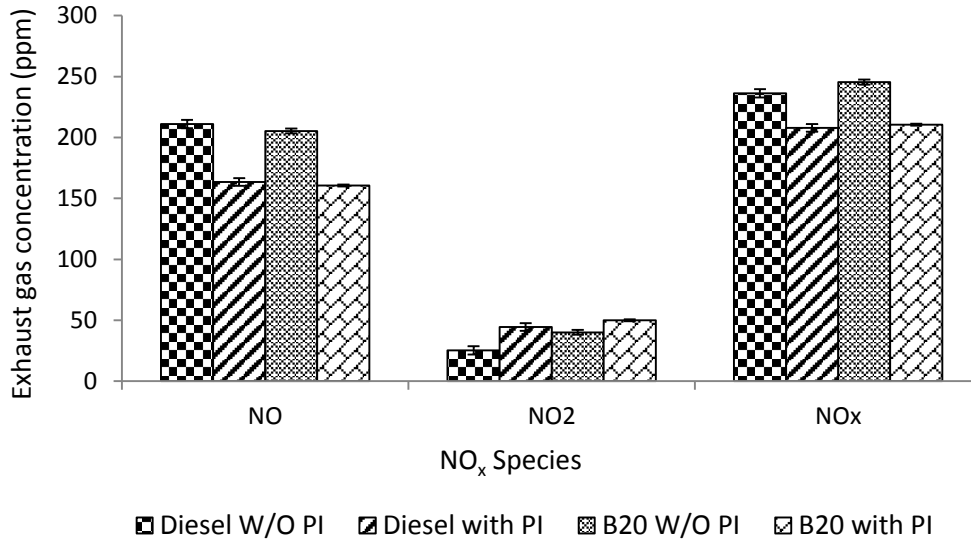
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A slight increase in  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) was measured for the B20 combustion with respect to diesel combustion for both injection strategies (Figure 11). This can be due to the slight increase of in-cylinder pressure as seen in Figure 2 and the presence of the chemically bound oxygen content in B20 as it has been previously reported in the case of oxygenated fuels [56]. In addition, the oxygen content and lower cetane number of butanol enhanced the burning rate (faster burning). Chen et al [57] reported similar trends in  $\text{NO}_x$  emissions from the combustion of n-butanol-diesel blends and suggested that this was a result of the ignition delay that was then led to wider high-temperature combustion region. Although both fuels have similar  $\text{NO}$  concentration, it seems that B20 blend has higher oxidation from  $\text{NO}$  to  $\text{NO}_2$  than diesel fuel due to the oxygen in the molecule. When post-injection was utilised the emissions of  $\text{NO}$  were decreased with simultaneously increasing in  $\text{NO}_2$  for both fuels (Figure 11). This is can be explained because a portion of  $\text{NO}$  was oxidised to  $\text{NO}_2$  by hydroperoxy radical ( $\text{HO}_2$ ) formed during post combustion [58] and because of the reduction of  $\text{NO}_x$  with some of the HCs post-injected. It was noted that the engine out  $\text{NO}_x$  emissions decreased under post-injection due to the possible formation of nitrated-hydrocarbon by reacting  $\text{NO}_x$  with radical HC [58].



302

303 **Figure 11.** NO<sub>x</sub> species concentrations of each gas species for with and without post-injection.

### 304 3.3 Brake specific fuel consumption and brake thermal efficiency

305 The brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) for both diesel  
 306 and butanol blends are summarized in Table 3. It was noticed that post injection strategy increased the  
 307 brake specific fuel consumption (BSFC) compared to that of main injection for both fuels. Moreover,  
 308 BSFC slightly increased with B20 for both injection strategies when compared to the diesel fuel. The  
 309 mean increase in BSFC for B20 when compared to the diesel under the same condition is 0.02811 and  
 310 0.02903 kg/kWh for without post-injection and with post-injection respectively. This is due to the lower  
 311 calorific value recorded for B20 (see Table 2) compared to the diesel fuel. Lapuerta et al. [59] and  
 312 Hajbabaei et al. [60] reported that the oxygenated fuels increases the BSFC mainly due to the reduced  
 313 calorific value when compared to the diesel. Furthermore, the smaller increase in BSFC for B20 its  
 314 compensated by its lower calorific value resulting in an increase in brake thermal efficiency efficiency.  
 315 This could be due to the oxygen content in the B20 which leads to improving the combustion and this  
 316 consistent with other researchers cited in introduction. It is clear from Table 3 that the post-injection  
 317 reduces brake thermal efficiency and increase the exhaust gas temperature (EGT) for both fuels.

318

**Table 3.** Brake specific fuel consumption and thermal efficiency.

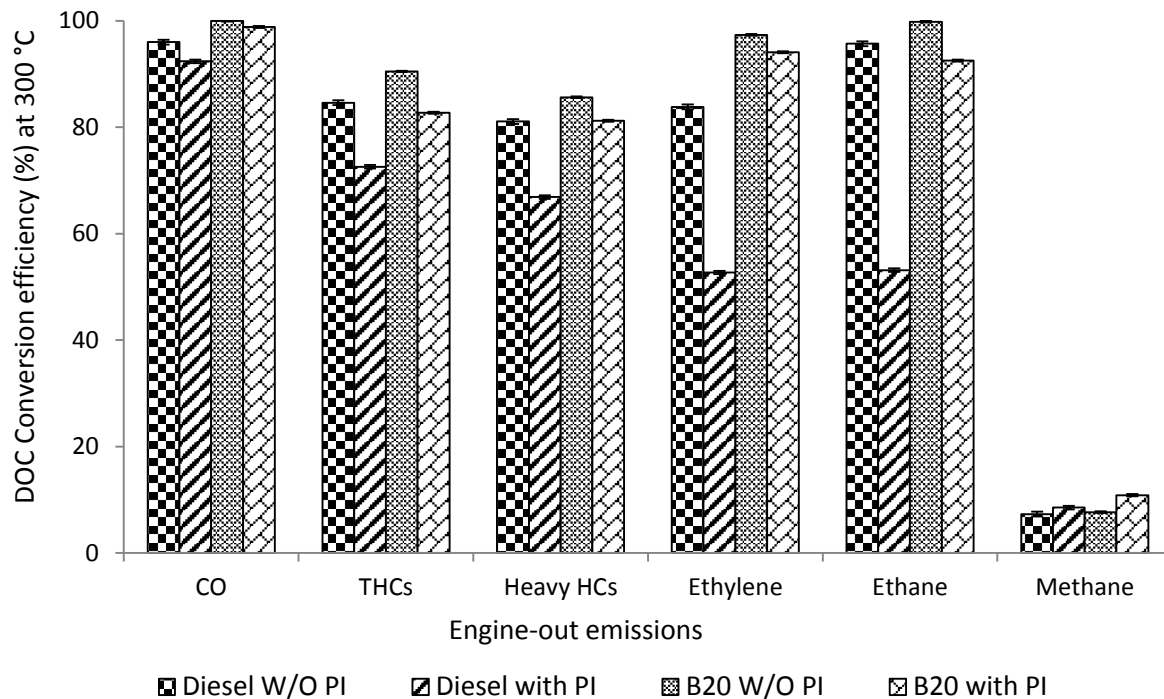
Fuel Parameters	Diesel fuel		B20	
	W/O PI	With PI	W/O PI	With PI
Brake specific fuel consumption, BSFC (kg/kWh)	0.3484	0.3645	0.3765	0.3935
Exhaust gas temperature, EGT (°C)	283	291	272	284
Brake thermal efficiency (BTE)	23.97	23.25	25.44	24.83



319 **3.4 Influence of fuel post-injection and fuel properties on DOC activity**

320 Combustion by-products in the exhaust gas are competing with each other to be adsorbed into  
321 the active sites of the catalyst [16, 22], effects that is highly depends on the temperature, flow  
322 conditions, space velocity and concentration and nature of the exhaust species. In active control  
323 aftertreatments such as diesel particulate filters (DPFs) the ability of the DOC to effectively oxidise  
324 the fuel and hydrocarbons and provide the required heat is important for the efficient operation of the  
325 engine system (including aftertreatment and engine fuel economy and emissions). The gas hourly  
326 space velocity (GHSV) and temperature of the DOC in this study were controlled and set at 35000 h<sup>-1</sup>  
327 and 300 °C, respectively in order to isolate the effect of exhaust gas composition.

328 The DOC is very effective in reducing CO in the engine exhaust from the combustion of both  
329 fuels, with the catalyst's CO conversion efficiency being higher for B20 blend. In the case of post-  
330 injection, the catalyst's CO oxidation efficiency was reduced (Figure 12), this is due to increased  
331 concentration of species that are now competing for the same number of active sites. The HC species  
332 presented in Figure 12 are light saturated (methane, ethane), light unsaturated (ethylene) and heavy  
333 HCs. The results confirm the differences in reactivity of the hydrocarbon species. Methane (CH<sub>4</sub>) as a  
334 short chain saturated hydrocarbon was the most difficult component to oxidise in the catalyst due to  
335 its low oxidation reactivity [23, 61]. Particularly, it can be observed that the conversion efficiency of  
336 methane over the catalyst was even lower than 10% at 300 °C for all the conditions studied. In addition,  
337 the increased concentration of heavier HCs and fuel in the exhaust that reaches the DOC leads to its  
338 non-selective poisoning (i.e. fouling or masking). The catalyst active sites are now occupied by the  
339 increased concentration of HCs and fuel that are interfering with the reactants transport phenomena to  
340 the catalyst active sites. This non-selective poisoning limits the catalytic surface area and obstructs  
341 access of the reactants to the pores. In this case the effect is reversible as for the B20 fuel combustion,  
342 the catalyst has the highest HC conversion efficiency at 300 °C compared with diesel fuel (Figure 12).  
343 This could be due to several reasons such as lower concentration of HC upstream the catalyst, higher  
344 reactivity of butanol and its derivatives, higher level of NO<sub>2</sub> emissions to catalytically oxidise the HC  
345 species [16, 62], lower PM/soot levels that can be responsible for blocking the active sites.



346

347 **Figure 12.** DOC activity at 300 °C.

348 **4. Conclusions**

349 The effect of fuel post-injection and butanol-diesel fuel blends (B20) on PM characteristics  
 350 (including size, fractal dimension, radius of gyration, and size of primary particles) and gaseous  
 351 emissions were analysed and their influence on DOC activity was investigated at exhaust temperature  
 352 of 300 °C. Due to reduced PM number concentration and HC emissions from the combustion of B20  
 353 the catalyst activity was improved. The HR-TEM analysis showed that the number of primary particles  
 354 of PM agglomerates emitted from B20 combustion was lower than that from the combustion of diesel  
 355 fuel. As B20 has oxygen-containing compounds, they contribute to inhibit the rate of soot formation  
 356 and to increase the rate of oxidation, resulting in particles with smaller average size and fractal  
 357 dimension. It is observed that the fuel post-injection has more clear benefits on PM reduction, resulting  
 358 in enhanced soot oxidation with similar trends on the morphology of agglomerates as the presence of  
 359 oxygenated compounds. HR-TEM analysis supports the results from SMPS and revealed that B20  
 360 produces particles with smaller average size compared to diesel fuel.

361 The fuel components as has been highlighted from the use of primary alcohols in this study,  
 362 can improve engine systems performance by providing a chain of beneficial effects; from the  
 363 combustion process to emissions formation processes to their abatement processes in the  
 364 aftertreatment systems. In this case the changes in fuels properties from the incorporation of butanol  
 365 into diesel fuel, led to cleaner combustion that eased species (i.e. HCs/fuel and engine out emissions)

366 oxidation in the DOC. These trends will favour the active control strategies in the aftertreatment  
367 systems and will positively impact on their performance (i.e. increase activity, improve durability) and  
368 overall engine fuel economy.

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## 381 **ABBREVIATIONS**

382 aTDC = after top dead centre  
383 B20D80 = butanol 20 %, and diesel 80%  
384 bTDC = before top dead centre  
385 BSFC = brake specific fuel consumption  
386 CAD = crank angle degree  
387 CI = compression ignition  
388 CO = carbon monoxide  
389 CO<sub>2</sub> = carbon dioxide  
390 d<sub>po</sub> = size of primary particles  
391 DOC = diesel oxidation catalyst  
392 DPF = diesel particulate filter  
393 EGT = exhaust gas temperature  
394 GHSV = gas hourly space velocity  
395 HC = hydrocarbons  
396 IMEP = indicated mean effective pressure  
397 NO = nitric oxide  
398 NO<sub>2</sub> = nitrogen dioxide  
399 NO<sub>x</sub> = nitrogen oxides  
400 n<sub>po</sub> = number of primary particles

401  $R_g$  = radius of gyration  
402 SMPS = scanning mobility particle sizer  
403 PSD = particulate size distribution  
404 PI = post-injection  
405 PM = particulate matter  
406 TEM = transmission electron microscopy  
407 THC = total hydrocarbons  
408 ULSD = ultra low sulfur diesel  
409 M-I = main injection  
410 W/O PI = without post-injection  
411 BTE = brake thermal efficiency

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