UNIVERSITY^{OF} BIRMINGHAM University of Birmingham Research at Birmingham

Role of alternative fuels on particulate matter (PM) characteristics and influence of the diesel oxidation catalyst

Fayad, Mohammed; Herreros, Jose; Martos, Francisco; Tsolakis, Athanasios

DOI: 10.1021/acs.est.5b02447

License: None: All rights reserved

Document Version Peer reviewed version

Citation for published version (Harvard):

Fayad, M, Herreros, J, Martos, F & Tsolakis, A 2015, 'Role of alternative fuels on particulate matter (PM) characteristics and influence of the diesel oxidation catalyst', *Environmental Science and Technology*, vol. 49, no. 19, pp. 11967–11973. https://doi.org/10.1021/acs.est.5b02447

Link to publication on Research at Birmingham portal

Publisher Rights Statement:

This document is the Accepted Manuscript version of a Published Work that appeared in final form in Environ. Sci. Technol, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see http://dx.doi/10.1021/acs.est.5b02447 See http://pubs.acs.org/page/policy/articlesonrequest/index.html.

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

•Users may freely distribute the URL that is used to identify this publication.

•Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.

•User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?) •Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

1 2

The Role of Alternative Fuels on PM Characteristics and Influence of the Diesel Oxidation Catalyst

3

Mohammed A. Fayad^a, Jose M Herreros^a, Francisco J. Martos^b, and Athanasios Tsolakis^{a*}

^a School of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

5 ^b Escuela Técnica Superior de Ingeniería Industrial, University of Málaga, 29071, Málaga, Spain

6 * Corresponding author. tel.: +44 (0) 121 414 4170, a.tsolakis@bham.ac.uk

7 Abstract

8 The influence of a platinum:palladium (Pt:Pd) based diesel oxidation catalyst (DOC) on the 9 engine out particulate matter (PM) emissions morphology and structure from the combustion of 10 alternative fuels including alcohol-diesel blends and rapeseed oil methyl ester (RME) biodiesel 11 was studied. PM size distribution was measured using a scanning mobility particulate 12 spectrometer (SMPS) and the PM morphology and microstructure including size distribution, 13 fractal geometry and number of primary particles was obtained using a high resolution 14 transmission electron microscopy (TEM).

It is concluded that the DOC does not modify the size or the microstructural parameters of the primary particulates that make up the soot agglomerates. The PM reduction seen in the DOC is due to the trapping effect, and oxidation of the PM's volatile components. The DOC performance in reducing gaseous e.g. carbon monoxide (CO), unburnt hydrocarbons (HCs) and PM emissions at low exhaust temperatures was improved from the combustion of alternative fuels due to the reduced level of engine out pollutants.

21 Keywords: diesel oxidation catalyst, alternative fuels, particulate matter, gaseous emissions.

22

24 Introduction

Due to recent popularity of the diesel powered vehicles, the increased particulate matter 25 (PM) emissions have become a major concern to human health and environment.^{1,2} Particulate 26 emissions from compression ignition (CI) engines are variable in size and morphology making 27 their control challenging. Therefore, understanding PM characteristics is likewise necessary for 28 the design of the control technologies like the particle traps. The morphology of the soot particles 29 is characterised by the size and the shape, and quantified by the fractal dimension.^{3,4} The 30 microstructure of the soot primary particulates is quantified by the interlayer spacing (d_{002}) and 31 the thickness (L_c) and width (L_a) of the graphene layer. It is reported that a large interlayer 32 spacing and small graphene layer thickness and width is representative of more disorder soot^{5,6} 33 (which have been seen as an indication of easier soot oxidation).^{7,8} Some studies have reported 34 that there is no direct correlation between the initial (fresh soot) microstructural parameters of 35 36 soot/PM and its oxidation readiness. This suggests that there are other parameters such as the functional groups present in the soot of the primary particulates that may affect its oxidation 37 characteristics.⁹ 38

There are methods to reduce pollutant emission and can be classified into different approaches: improved fuels quality and, use of alternative fuels such as biofuels can enhance/modify the combustion process and reduce the engine out pollutants leading to improved aftertreatment systems (e.g.diesel oxidation catalyst-DOC) performance.¹⁰⁻¹³

Alcohol fuels are commonly used in spark ignition engines, but their blends with diesel fuel have also been considered in compression ignition engines and emission benefits have been reported.^{11,13} Some properties of alcohols such as its short chain and oxygen content can provide significant reduction in unburnt hydrocarbons (HCs), PM, and carbon monoxide (CO) emissions.^{14,15} Butanol has been considered as a feasible fuel for use also in diesel engines due to its higher energy density, higher miscibility in diesel fuel and better blending stability than
ethanol.^{15,16} A ternary blend alcohol-diesel-biodiesel is considered to compensate for the low
cetane number and lubrication properties of the alcohol fuels. On the other hand, the engine
performance, exhaust emission, lubricity and fuel miscibility are affected by variation in
biodiesel composition in fuel blend.^{17, 18}

One of the approaches to meet the emissions regulations is the use of advances aftertreatment 53 units such as selective catalytic reduction (SCR) for the control of NO_x emissions; diesel 54 particulate filters (DPF) to trap PM¹⁹; and DOC to eliminate CO and HC emissions and to 55 generate NO₂ for use in passive regeneration of the DPF and to promote NO_x reduction in the 56 selective catalytic reduction (SCR) systems.¹⁰ There are some exhaust conditions where catalytic 57 reactions can be promoted and inhibited and are dependant on the presence and quantity of 58 59 different species in the engine exhaust. DOC with high suitable loadings of a catalytic material, such as platinum and high cell density, could also physically trap and oxidise the volatile 60 component of PM.^{11,20,21} Furthermore, the majority of those studies are performed only for 61 conventional diesel fuel²¹⁻²³ and the issues associated to particulate matter oxidation/reduction in 62 the DOC have not been in depth addressed. Therefore, the main objective of this study is to 63 64 understand the combined effect of the fuel and DOC on the size, morphology and microstructure of the soot agglomerates. The exhaust emission interactions (obstruction/promotion) for CO, HC 65 and NO oxidation on a DOC from the combustion of butanol blends (16 % butanol, 15% RME 66 and 69% diesel), rapeseed oil methyl ester (RME) and diesel fuelling were also investigated. 67

68

Experimental set-up and methodology

The schematic diagram of the diesel engine and aftertreatment system set-up is shown in
figure S1 (see supporting information). The catalyst activity studies have been carried-out using

exhaust from a naturally aspirated single cylinder four stroke, direct injection diesel engine; the
main specifications of diesel engine are presented in table S1. Intake air flow, fuel consumption,
exhaust pressure and exhaust temperature were also measured.

Ultra low sulphur diesel (ULSD) fuel, biodiesel derived from rapeseed oil (RME) fuel 74 used in this study and was supplied by Shell Global Solutions UK. Butanol used in blending with 75 diesel fuel and RME and was purchased from Fisher Scientific. The physical and chemical 76 properties of the pure components were calculated or obtained from provided company or 77 publications (Table 1). This blend was selected due to the favourable fuel blend properties and 78 emissions results when used in compression ignition engines according to Sukjit et al.¹¹ The 79 properties of the fuel blends are presented in Table 1.^{11,18} As shown in Figure S2 (see supporting 80 information), the selected fuel blends tested were B16R15D (16 % butanol, 15% RME and 69% 81 82 diesel).

The DOC used in this research is a 120 g/ft³ Platinum: Palladium (weight ratio 1:1) with alumina and zeolite washcoat (2.6 g/in³ loading) on a cordierite honeycomb monolith. Diameter, length and wall thickness of the DOC are 25.4 mm, 91.4 mm and 4.3 mil respectively with 400 cells per in². The DOC used in this study was supplied by Johnson Matthey Plc.

Gaseous emissions emitted from the diesel engine such as CO, NO_x , and total hydrocarbons HCs, were measured using a MultiGas 2030 FTIR spectrometry based analyzer. A scanning mobility particle sizer (SMPS) was employed to measure the size of particulate matter emissions emitted from the diesel engine. A model TSI SMPS 3080 particle number and size classifier with thermodiluter was utilized to evaluate the two parameters of the PM emissions which it is the number of concentration and size. The thermodiluter was fitted with air temperature at 150 °C and dilution ratio was set at 1:200 for all tests.

94 The soot particulate samples used in morphology studies have been collected from the exhaust gas stream in different points in 3 mm copper grids attached to a sampling probe. These 95 soot particulates were analysed using a high resolution transmission electron microscopy (HR-96 TEM) with a Phillips CM-200 microscope which have high resolution about 2 Å at an 97 accelerating voltage of 200 kV. The morphological parameters of the agglomerates (radius of 98 gyration, number of primary particles and fractal dimension) and microstructural parameters 99 (interlayer spacing and thickness of graphene layer) were obtained from the TEM micrographs 100 using a homemade Matlab software (digital image analysis software).^{24, 25} 101

102 All the tests were carried out in steady state at an engine speed of 1500 rpm with an 103 engine load of 4 bar IMEP representing approximately 45 % of the maximum load. The DOC 104 was loaded inside a furnace to independently study the effects of temperature, space velocity, and 105 exhaust composition and exposed to the engine exhaust keeping a gas space velocity of 35000/h 106 and a heating temperature of about 2 $^{\circ}$ C/min.

107 **Results and discussions**

108 DOC effect on Particulate Matter

Particulate matter size distribution and morphology studied from the combustion of the different fuels has been carried out in order to identify the influence of the DOC in the (i) oxidation of gaseous hydrocarbons which can later be nucleate, adsorbed or condensed to form particulate matter, (ii) oxidation or desorption of the hydrocarbon already present onto the particulate matter, (iii) agglomeration of particulates that may lead in increasing the number of particulates and the size of the agglomerates, (iv) trapping effect due to the deposition by diffusion of particulates in the DOC channels and (v) oxidation of soot particulates.

The particulate number concentration for diesel fuel combustion is significantly higher for all the particulate sizes compared to RME and the butanol blend combustion as depicted in Figure S3 (see supporting information). This lower particulate number concentration in the case of oxygenated fuels has been previously reported in the literature.²⁶ The oxygen content in the ester group of RME and in the hydroxyl group of butanol are the main reasons to justify the lower engine out PM emissions.

Figures 1a & b show the number of particulate matter reduced in the DOC from the combustion of the four fuels when the catalyst inlet temperature is 400 and 500 $^{\circ}$ C, respectively. For temperatures lower than 400 $^{\circ}$ C (i.e. 100 $^{\circ}$ C, 200 $^{\circ}$ C, 300 $^{\circ}$ C) the influence of DOC on PM was the same to 400 $^{\circ}$ C and the results are not shown to avoid duplication. The reduction in the number of particulates in the DOC reaches a constant level around 30% for particulates larger than 50 nm.

The average particulate electrical mobility diameter (obtained with the SMPS) and 128 average gyration radius (obtained from the TEM images, Figure S4 included in supporting 129 130 information) have been compared in Figure 2. Furthermore, the number of primary particulates which compose the aggregates is also plotted in Figure 2.In all the cases (Figure 2) the values of 131 the average mobility diameter and gyration diameter are similar and of the same rank, even 132 though they are based on different measurement methods (e.g. mobility diameter is obtained 133 from particulates after dilution, while TEM analysis is obtained directly from exhaust 134 agglomerates). The average particulate size for butanol blend and RME is lower than in the case 135 of diesel fuel combustion. However, the smaller average agglomerate size of the particulates 136 emitted with RME and the butanol blend is not due to an increase in the number of small 137 particulates but due to a significant reduction in the number of larger ones.^{11,18} 138

There is also an increase in the average particulate size along the catalyst trend that is 139 supported by the mobility diameter (SMPS) and to lesser extent by the radius of gyration results 140 141 obtained by TEM. This increase is obtained at both 400 and 500 °C temperatures for all the studied fuels. This increase in the mean particulate diameter is due to the higher diffusion losses 142 143 associated to the particulates of smaller diameters (below 20 nm) as well as due to the collision of particulates in the DOC channels. This leads to the formation of larger size agglomerate from 144 145 the high number of primary particles as it was also confirmed from the TEM results (Figure 2). 146 The trapping effect of the small particulates is the major effect in the exhaust gas from the 147 combustion RME and butanol blends as the agglomerates analysed with TEM upstream and downstream the catalyst have similar size (Figure 2). However, the increase in the agglomerate 148 149 size in the case of diesel fuel is dominated by the collision and further aggregation between them 150 as it is shown in the TEM results (Figure 2). The higher number of particulates in the case of diesel fuel combustion increases the likelihood of collisions between them. The larger reduction 151 152 in the number of particulate matter when the DOC temperature is 500 °C with respect to 400 °C 153 in the case of RME cannot be due to the oxidation of gas phase hydrocarbon as the DOC oxidation efficiency was the same for both temperatures. It could be interpreted as an indication 154 of the oxidation of organic material already contained in the particulates or an indication of soot 155 156 oxidation activity due to the lower soot oxidation temperature from RME combustion as it has been previously reported.^{26,27} This should be confirmed by the morphological and 157 158 microstructural results discussed below.

The fractal dimension (D_f) obtained for all the conditions are in the typical range of diesel particulates (1.7-1.8) which is characteristic of diffusion limited aggregation mechanism growth. ²⁸ According to the results, the fractal dimension of the aggregates of

particulates produced from the combustion of diesel fuel is larger than those produced from the combustion of RME, and the butanol blend (Figure 3). Soot aggregates from the diesel fuel combustion have a more pronounced spherical shape compared to the rest of the fuels.^{24,28} Therefore, it is expected that the particulates emitted from the alternative fuels to be easier to be trapped in the filters due to their chain shape morphology.

167 The PM shape was also changed over the DOC due to the aggregation as well as thermal 168 restructuration of the agglomerates due to the temperature increase within the catalyst. As a 169 result, the particles downstream the DOC have slightly more spherical shape, especially in the 170 case of those emitted from diesel fuel. It can be noted that the DOC has considerable reduction 171 and a significant influence on the size and concentration of particulate emissions, which in turn 172 enables to reduce tail pipe PM emission.

The size of primary particulates (d_{po}) and the microstructural parameters for all the 173 174 studied fuels has also been investigated and presented in Figure S5 (see supporting information). A statistically significant number of primary particulates (around 150-200) 175 for each fuel and condition (before and after the DOC) has been measured to produce the 176 fitted lognormal/normal distribution (Figure S5 included in supporting information) and 177 calculate the mean primary particulate size (Figure 4). It can be obtained that the size of 178 primary particulates is bigger in the case of diesel fuel combustion, while the smallest 179 primary particulates size are obtained from the combustion of butanol blend. This is a 180 result of the lower rate of production of soot precursors, which limits the soot formation 181 182 and increases the soot oxidation rate during the combustion process of the oxygenated 183 fuels. This result together with the morphology results demonstrates that the smaller size agglomerates in the case of oxygenated fuels is due to the lower number of primary 184

particulates as well as the smaller size of the primary particulates which composed the agglomerates. It can also be concluded that the DOC does not modify the primary particulate size in any of the fuels. This result supports the idea that the DOC only affects the particulate agglomerates rather than the primary particulates which would need higher temperatures and residence time in the catalyst to be oxidised.

PM microstructure (Figure 5) has been quantified by the average interlayer spacing 190 (d_{002}) and average thickness of the graphene layer which composed the soot primary 191 particulates. It is shown that the interlayer spacing from the soot produced from RME and 192 butanol blends combustion is smaller than those found in the soot produced from diesel 193 combustion (Figure 5). However, there are no statistical significant differences between the 194 average thicknesses of the graphene layer derived from the combustion of the studied 195 196 fuels. The smaller interlayer spacing for the soot derived from oxygenated fuels is an indication of a more ordered structure being supported by the literature.¹⁰ Figure 5 also 197 shows that the DOC does not produce any statistical significant effect to the microstructural 198 parameters obtained from the PM of all the fuels. 199

Based on the morphology and microstructural results of particulate matter upstream and downstream the diesel oxidation catalyst, it can be concluded that DOC oxidises the adsorbed hydrocarbons on PM (effect ii), leads to agglomeration of particulates (effect iii) and traps by diffusion some of the solid particulates (effect iv). However, the DOC it is not able to oxidise the soot (effect v). It is proposed that the residence time between the soot and the catalysed active sites within the DOC is not enough to oxidise it irrespective of the fuel used.

207 **<u>CO reduction in the DOC</u>**

The CO and HCs engine output emissions from the combustion of conventional diesel 208 fuel are higher compared to the rest of the tested fuels (Figure S6 included in supporting 209 information). The high level of CO and HCs for diesel combustion hampers the CO adsorption 210 onto the catalyst (zeolites) at low exhaust gas temperatures.¹⁰ leading to a delay in the start of CO 211 light-off compared to the other fuels (Figure 6). On the contrary, the lower engine output HC and 212 CO concentration from the combustion of RME and alcohol blend (Figure S6 included in 213 supporting information) reduces the possibility for obstruction from CO and HC competition and 214 215 improved the catalyst CO light-off. At low temperatures, the CO oxidation in the DOC is kinetically limited (poor accessibility to active sites by other component inhibition).²⁹ 216

Once the oxidation has started, there are some plateaus in the CO light-off curves for 217 most of the fuels (around 100-150 °C). At high exhaust temperatures, CO is not 218 219 thermodynamically limited and the heat release from its oxidation increases the local temperature of the catalyst. This higher active site temperature helps the oxidation of CO (Figure 6), 220 221 especially in the case of diesel fuel combustion where the level of CO emission is higher. Moreover, this higher rate of CO oxidation for the case of diesel fuel at this temperature could be 222 due to high hydrocarbon depletion as shown in Figure 7. At higher temperatures (approximately 223 180 °C), the CO oxidation in the DOC catalyst for diesel combustion reaches 100 % at lower 224 temperature compares to the rest of the fuels, especially for RME (Figure 6). The exhaust from 225 the RME combustion has the lowest level of CO and the highest levels of NO_x leading to 226 reduced exothermic and increased competition for active sites between CO and NO. 23 227

228 HC's reduction in the DOC

The low temperature hydrocarbon conversion seen in the DOC is due to the trapping effect by the zeolites ('virtual conversion').²³ When temperature increases and the conversion efficiency for CO is high; the catalyst active sites become available for HCs
adsorption and oxidation. It can be seen that HCs oxidation for all the fuels increased once
CO was fully oxidised (Figure 6 and Figure 7).

234 The lowest HCs conversion efficiency over the DOC occurs for the case of diesel fuel combustion. This is due to the higher upstream concentration of engine out aromatic 235 hydrocarbons which have been reported to be more difficult to be adsorbed and oxidised.^{18,} 236 ^{22, 30, 31} Meanwhile, higher HC conversion in the DOC noted when exhaust gas from the 237 combustion of the RME was used and this is due to the absence of aromatic hydrocarbons 238 in the fuel structure. Moderate HC conversion is obtained when exhaust gas from for the 239 combustion alcohol blends was used and this is due to the large presence of diesel in the 240 fuel blend, partially compensated by the presence of the alcohol. 241

242 <u>NO to NO₂ oxidation in the DOC</u>

The oxidation of NO to produce NO_2 in the DOC (Figure 8) is influenced by the different concentrations of CO, NO and by the concentration and type of HCs. It can be observed that at low temperature the NO_2 concentration downstream the DOC is lower than the engine output NO_2 . This is the effect of NO_2 reacting with CO and HC in the DOC catalyst.

The increase in the NO₂ concentration downstream the catalyst starts around the same temperatures (approximately 220 °C) for all the studied cases, once the CO has been completed oxidised by oxygen in the catalyst active sites. Hence, it is evident the inhibition of CO on NO₂ production occupying the catalyst active sites as well as the consumption of any NO₂ created by reaction with CO and HCs to form CO₂.

It is noticeable the higher NO₂ concentration downstream the catalyst at 253 temperatures below 350 °C was seen in the case of butanol combustion. The formation of 254 some very active oxygenated hydrocarbon components which could be formed in the 255 256 catalyst can enhance NO₂ production. A similar effect has been already reported in the case of Ag/Al₂O₃ catalyst where the formation of NO₂ is highly promoted under the addition of 257 alcohol fuels.^{32,33} At temperatures higher than 350 °C the NO₂ production is not further 258 increasing forming a plateau as the NO₂ production from NO oxidation is thermodynamic 259 260 limited.³⁴

261 Influence of DOC technology on PM emissions from the combustion of alternative fuels

The purpose of the present work was to investigate the effects of a diesel oxidation catalyst on particulate matter characteristics and gaseous emissions from the combustion of alternative fuels. This study gives an insight regarding of the effects of alternative fuels on the DOC performance over (i) particulate matter reduction/modification, (ii) pollutant emissions oxidation such as CO and THCs to CO_2 and H_2O and (iii) NO oxidation to NO_2 which can be further used in the catalytically reduction of NO_x in the SCR or in the DPFs for passive regeneration.

The combustion of alternative fuels produces lower emissions of unburnt hydrocarbons, CO and PM number concentration which enhances the catalyst activity at lower temperatures by limiting the CO and HCs inhibition effect and DOC performance in long term operation by reducing the PM accumulation effect. PM agglomerates and their primary particles emitted from the combustion of alternative fuels are in average smaller and with a lower fractal dimension, thus are being easier to be trapped or oxidised. It has to be noticed that the average smaller size of the agglomerates emitted from the combustion of alternative fuels is due to the production of lower number of large particulates rather than a high number of small particulates not beingdetrimental for the environment and/or downstream diesel particulate filter.

SMPS and TEM analysis revealed that the PM filtration efficiency in the DOC is higher for the small particles and that there is a PM aggregation process that takes place within the DOC. Furthermore, the DOC does not modify the primary particulates size and microstructural parameters for any of the studied fuels. Therefore, it is thought that the DOC only has a trapping effect on soot and oxidises the PM volatile components, while a longer residence time is needed to oxidise the soot.

284 Acknowledgements

The Iraqi Government and University of Technology in Baghdad is gratefully acknowledged for 285 the PhD scholarship and maintenance grant for Mr. Mohammed Fayad. Innovative UK (The 286 287 Technology Strategy Board, TSB) and EPSRC for supporting this work with the projects (CREO: ref. 400176/149) and (EP/G038139/1), respectively. F.J. Martos expresses thanks to the 288 University of Malaga for supporting his research stay at the University of Birmingham. With 289 thanks to Advantage West Midlands and the European Regional Development Fund, funders of 290 the Science City Research Alliance Energy Efficiency project – a collaboration between the 291 292 Universities of Birmingham and Warwick.

293 ASSOCIATED CONTENT

294 Supporting Information

Figure S1 shows the simplified schematic diagram of engine and DOC system, while Figure S2 shows the ternary diagrams representing the fuel test blends. Figure S3 shows the engine output particulate size distribution for different fuels upstream the diesel oxidation catalyst. TEM and

- HR-TEM micrographs of particulates matter are shown in Figure S4 and Figure S5, respectively.
- Engine output gaseous emissions for the different studied fuels are depicted in Figure S6. Table
- 300 S1 shows the engine specifications. This information is available free of charge via the Internet
- 301 at http://pubs.acs.org.

302 ABBREVIATIONS

- 303 B16R15D = butanol 16 %, RME 15% and Diesel 69%
- CI = compression ignition
- $305 \quad CO = carbon monoxide$
- $CO_2 = carbon dioxide$
- $d_{002} = interlayer spacing$
- 308 DOC = diesel oxidation catalyst
- $D_f = fractal dimension$
- 310 DPF = diesel particulate filter
- HC = hydrocarbons
- 312 IMEP = indicated mean effective pressure
- 313 $L_c =$ graphene layer thickness
- NO = nitric oxide
- $NO_2 = nitrogen dioxide$
- $NO_x = nitrogen oxides$
- 317 $n_{po} =$ number of primary particles
- 318 $R_g = gyration radius$
- 319 RME = rapeseed oil methyl ester
- 320 SCR = selective catalytic reduction
- 321 SMPS = scanning mobility particle sizer
- 322 PM = particulate matter
- 323 TEM = transmission electron microscopy
- THC = total hydrocarbons
- 325 ULSD = ultra low sulfur diesel

326

327 **References**

- 328[1]Diesel Engine Exhaust Carcinogenic, Press release no. 213; International Agency for329Research on Cancer, 2012; http://www.iarc.fr/en/media-centre/pr/2012/pdfs/pr213_E.pdf.
- Geller, M. D.; Sardar, S. B.; Phuleria, H.; Fine, P. M.; Sioutas, C. Measurements of
 particle number and mass concentrations and size distributions in a tunnel environment. *Environ. Sci. Technol.* 2005, 39 (22), 8653-8663.
- Kimijima T.; Haneishi T.; Okabe H. Effect of soot on anti-wear properties of marine
 diesel engine oils. *J Jpn Soc Tribologis*. 1994, 39, 337-344.
- Meakin, P.; Donn, B; and Mulholland, G.W. 'Collisions between point masses and fractal aggregates', *Langmuir*. 1989, 5, 510-518.
- Ishiguro, T.; Suzuki, N.; Fujitani, Y.; Morimoto, H. Microstructural changes of diesel
 soot during oxidation. *Combust Flame*. 1991, 85, 1-6.
- Liati, A.; Eggenschwiler, P. D. Characterization of particulate matter deposited in diesel
 particulate filters: visual and analytical approach in macro-, micro- and nano scales. *Combust Flame*. 2010,157, 1658-1670.
- Su, D.S.; Jentoft, R.E.; Müller, J. O.; Rothe, D.; Jacob, E.; Simpson, C.D.; Tomovic, Z.;
 Müllen, K.; Messerer, A.; Pöschl, U.; Niessner, R.; Schlögl, R. Microstructure and
 oxidation behaviour of Euro IV diesel engine soot: a comparative study with synthetic
 model soot substances. *Catal Today*. 2004, 90, 127-132.
- [8] Vander, Wal, R.; Tomasek, A.J. Soot nanostructure: dependence upon synthesis
 conditions. *Combust Flame*. 2004, 136, 129-140.
- Al-Qurashi, K.; Boehman, A. L. Impact of exhaust gas recirculation (EGR) on the
 oxidative reactivity of diesel engine soot. *Combust Flame*. 2008, 155, 675-695.
- [10] Lefort, I.; Herreros, JM.; Tsolakis, A. Reduction of low temperature engine pollutants by
 understanding the exhaust species interactions in a diesel oxidation catalyst. *Environ. Sci. Technol.* 2014, 48, 2361-2367.
- Sukjit, E.; Herreros, J. M.; Dearn, K. D.; García-Contreras, R.; Tsolakis, A. The effect of
 the addition of individual methyl esters on the combustion and emissions of ethanol and
 butanol-diesel blends. *Energy*. 2012, 42 (1), 364-374.
- Choi, B.; Jiang, X. Individual hydrocarbons and particulate matter emission from
 a turbocharged CRDI diesel engine fuelled with n-butanol/diesel blends. *Fuel.* 2015,
 154, 188-195.
- Gunfeel, M.; Yonggyu, L.; Kyonam, C.; Dongsoo, J. Emission characteristics of diesel,
 gas to liquid, and biodiesel-blended fuels in a diesel engine for passenger cars. *Fuel*.
 2010, 89 (12), 3840-3846.
- 362 [14] Zhang, Z, H.; Balasubramanian, R. Effects of oxygenated fuel blends on
 363 carbonaceous particulate composition and particle size distributions from a stationary
 364 diesel engine. *Fuel.* 2015, 141, 1-8.
- Rakopoulos, D. C.; Rakopoulos, C. D.; Papagiannakis, R. G.; Kyritsis, D. C. Combustion
 heat release analysis of ethanol or nbutanol diesel fuel blends in heavy-duty DI diesel
 engine. *Fuel.* 2011, 90 (5), 1855-1867.

- 368 [16] Octavio Armas, O.; García-Contreras, R.; Ramos, A. Pollutant emissions from engine
 369 starting with ethanol and butanol diesel blends. *Fuel Process Technol.* 2012, (100) 63-72.
- Selvan, T ; Nagarajan, G. Combustion and Emission Characteristics of a Diesel Engine
 Fuelled with Biodiesel Having Varying Saturated Fatty Acid Composition. *Int J Green Energy.* 2013, 10 (9), 952-965.
- Hueseyin, A.; Cumali, I. Effect of ethanol blending with biodiesel on engine performance
 and exhaust emissions in a CI engine. *Appl Therm Eng.* 2010, 30 (10), 1199-1204.
- Herner, J. D.; Hu, S.; Robertson, W. H.; Huai, T.; Collins, J. F.; Dwyer, H.; Ayala, A.
 Effect of Advanced Aftertreatment for PM and NOx Control on Heavy-Duty Diesel
 Truck Emissions. *Environ. Sci. Technol.* 2009, 43 (15), 5928-5933.
- Katare, SR.; Laing, PM. Hydrogen in diesel exhaust: effect on diesel oxidation catalyst
 flow reactor experiments and model predictions. *SAE Paper*. 2009, 2009-01-1268.
- [21] Ko, A.; Kim, J.; Choi, K.; et al. Experimental study of particle emission characteristics of
 a heavy-duty diesel engine and effects of aftertreatment systems: Selective catalytic
 reduction, diesel particulate filter, and diesel particulate and NO_x reduction. *J. Aut. Eng.* 2012; 226 (12), 1689-1696.
- Katare, S.; Patterson, J.; Laing, P. Aged DOC is a Net Consumer of NO2: Analyses of
 Vehicle, Engine-dynamometer and Reactor Data. *SAE Paper* 2007, 2007-01-3984.
- Lafossas, F.; Matsuda, Y.; Mohammadi, A.; Morishima, A.; Inoue, M.; Kalogirou, M.;
 Koltsakis, G.; Samaras, Z. Calibration and validation of a diesel oxidation catalyst model:
 From synthetic gas testing to driving cycle applications. *SAE Int. J. Engines.* 2011, 4 (1),
 1586-1606.
- Lapuerta, M.; Ballesteros, R.; Martos, F. J. A method to determine the fractal dimension
 of diesel soot agglomerates. *J Colloid Interf Sci.* 2006, 303, 149-158.
- Iz5] Lapuerta M.; Martos F.J.; Martín–González G. Geometrical determination of the
 lacunarity of agglomerates with integer fractal dimension. *J Colloid Interf Sci.* 2010, 346,
 23-31.
- Song, J.; Alam, M.; Boehman, A. L.; Kim, U. Examination of the oxidation behaviour of
 biodiesel soot. *Combust. Flame.* 2006, 146, 589-604.
- Boehman, A. L.; Song, J.; & Alam, M. "Impact of Biodiesel Blending on Biodiesel Soot and the Regeneration of Particulate Filters", *Energy Fuels*. 2005, 1857-1864.
- Meakin, P.: In "On growth and Form," edited by Stanley and Ostrowsky, MartinusNijhoff Publishers, Boston. **1986**, 111-135.
- 401 [29] Stevanovic, S.; Miljevic, B.; Surawski, N. C.; Fairfull-Smith, K. E.; Bottle, S. E.; Brown,
 402 R.; and Ristovski, Z. D. Influence of Oxygenated Organic Aerosols (OOAs) on the
 403 Oxidative Potential of Diesel and Biodiesel Particulate Matter. *Environ. Sci. Technol.*404 2013, 47 (14), 7655-7662.
- 405 [30] Hori, M. Experimental study of nitrogen dioxide formation in combustion systems. *Symp*406 (*Int*) Combust. 1988, 21(1), 1181-1188.

- 407 [31] Ladommatos, N.; Abdelhalim, S. M.; Zhao, H. Effects of exhaust gas recirculation
 408 temperature on diesel engine combustion and emissions. Proc. Inst. Mech. Eng. *J. Aut.*409 *Eng.* 1998, 212 (6), 479-500.
- 410 [32] Herreros, J. M.; George, P.; Umar, M.; Tsolakis, A. Enhancing selective catalytic
 411 reduction of NO_x with alternative reactants/promoters. *Chem. Eng.* J. 2014,252, 47-54.
- 412 [33] Johnson, W.L.; Fisher, G.B.; Toops, T.J. Mechanistic investigation of ethanol SCR of
 413 NO_x over Ag/Al2O3, *Catal. Today.* 2012,184 (1), 166-177.
- 414 [34] Cooper, B.; and Thoss, J. "Role of NO in Diesel Particulate Emission Control," *SAE*415 *Technical Paper*. 1989, 890404.

Tables Caption

Table 1. Specification of tested fuels [11, 18].

Properties	ULSD 100%	RME 100%	Butanol	B16R15D (butanol blend)
Chemical formula	$C_{14}H_{26.1}$	$C_{19}H_{35.3}O_2$	C ₄ H ₉ OH	$C_{11}H_{21.4}O_{0.5}$
Cetane number	53.9	54.74	17	
Latent heat of vaporization (kJ/kg)	243	216	58	
bulk modulus (MPa)	1410	1553	1500	
density at 15 °C (kg/m ³)	827.1	883.7	809.5	835.2
kinematic viscosity at 40 °C (cSt)	2.70	4.53	2.23	2.54
lower calorific value (MJ/kg)	43.11	37.80	33.12	39.97
lubricity at 60 °C(µm)	312	205	620	405
C (wt %)	86.44	77.09	64.78	81.56
H (wt %)	13.56	12.07	13.63	13.34
O (wt %)	0	10.84	21.59	5.08
O from OH group (wt %)	0	0	21.59	3.36
Boling point (°C)	-	-	117.5	
50% distillation (°C)	264	335	117	
90% distillation (°C)	329	342	117	

Table 1.

Figures Caption

Figure 1. Particulate matter reduction in the DOC for different fuels for (a) 400 °C, (b) 500 °C.

Figure 2. Particle size of SMPS results Vs. Gyration radius (R_g) and number of primary particles (n_{po}) for (a) diesel fuel, (b) butanol blend (c) RME.

Figure 3. Fractal dimensions of particulates matter from TEM for all fuel tested.

Figure 4. Size of primary particulate (d_{po}) for all fuel tested.

Figure 5. Particulate matter microstructure, high resolution TEM micrograph, interlayer spacing (d_{002}) and graphene layer thickness (L_c) .

Figure 6. CO light-off curves from exhaust gas produced for different fuels.

- Figure 7. DOC conversion efficiency for THC.
- Figure 8. NO and NO₂ catalyst outlet concentration from engine operation.



Figure 1.



Figure 2.



a DOC: after DOC, b DOC: before DOC

Figure 3.



a DOC: after DOC, b DOC: before DOC

Figure 4.



a DOC: after DOC, b DOC: before DOC

Figure 5.



Figure 6.



Figure 7.



Figure 8.

TOC/Abstract art

