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

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Abstract

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

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

Introduction

Due to recent popularity of the diesel powered vehicles, the increased particulate matter (PM) emissions have become a major concern to human health and environment.[1,2] Particulate emissions from compression ignition (CI) engines are variable in size and morphology making their control challenging. Therefore, understanding PM characteristics is likewise necessary for the design of the control technologies like the particle traps. The morphology of the soot particles is characterised by the size and the shape, and quantified by the fractal dimension.[3,4] The microstructure of the soot primary particulates is quantified by the interlayer spacing (d_{002}) and the thickness (L_c) and width (L_a) of the graphene layer. It is reported that a large interlayer spacing and small graphene layer thickness and width is representative of more disorder soot[5,6] (which have been seen as an indication of easier soot oxidation).[7,8] Some studies have reported that there is no direct correlation between the initial (fresh soot) microstructural parameters of 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 characteristics.[9]

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 units such as selective catalytic reduction (SCR) for the control of NO_x emissions; diesel particulate filters (DPF) to trap PM[19]; and DOC to eliminate CO and HC emissions and to generate NO_2 for use in passive regeneration of the DPF and to promote NO_x reduction in the selective catalytic reduction (SCR) systems.[10] There are some exhaust conditions where catalytic reactions can be promoted and inhibited and are dependant on the presence and quantity of 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 component of PM.[11,20,21] Furthermore, the majority of those studies are performed only for conventional diesel fuel[21-23] and the issues associated to particulate matter oxidation/reduction in the DOC have not been in depth addressed. Therefore, the main objective of this study is to 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 and NO oxidation on a DOC from the combustion of butanol blends (16 % butanol, 15% RME and 69% diesel), rapeseed oil methyl ester (RME) and diesel fuelling were also investigated.

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 used in this study and was supplied by Shell Global Solutions UK. Butanol used in blending with diesel fuel and RME and was purchased from Fisher Scientific. The physical and chemical properties of the pure components were calculated or obtained from provided company or publications (Table 1). This blend was selected due to the favourable fuel blend properties and emissions results when used in compression ignition engines according to Sukjit et al.[11] The properties of the fuel blends are presented in Table 1.[11,18] As shown in Figure S2 (see supporting information), the selected fuel blends tested were B16R15D (16 % butanol, 15% RME and 69% diesel).

The DOC used in this research is a 120 g/ft^3 Platinum: Palladium (weight ratio 1:1) with alumina and zeolite washcoat (2.6 g/in^3 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 in^2. 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.

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 soot particulates were analysed using a high resolution transmission electron microscopy (HR-TEM) with a Phillips CM-200 microscope which have high resolution about 2 Å at an accelerating voltage of 200 kV. The morphological parameters of the agglomerates (radius of gyration, number of primary particles and fractal dimension) and microstructural parameters (interlayer spacing and thickness of graphene layer) were obtained from the TEM micrographs using a homemade Matlab software (digital image analysis software).[24, 25]

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

Results and discussions

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 average gyration radius (obtained from the TEM images, Figure S4 included in supporting 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 the average mobility diameter and gyration diameter are similar and of the same rank, even though they are based on different measurement methods (e.g. mobility diameter is obtained from particulates after dilution, while TEM analysis is obtained directly from exhaust agglomerates). The average particulate size for butanol blend and RME is lower than in the case of diesel fuel combustion. However, the smaller average agglomerate size of the particulates emitted with RME and the butanol blend is not due to an increase in the number of small particulates but due to a significant reduction in the number of larger ones.[11,18]

There is also an increase in the average particulate size along the catalyst trend that is supported by the mobility diameter (SMPS) and to lesser extent by the radius of gyration results 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 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 the high number of primary particles as it was also confirmed from the TEM results (Figure 2). The trapping effect of the small particulates is the major effect in the exhaust gas from the 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 size in the case of diesel fuel is dominated by the collision and further aggregation between them 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 in the number of particulate matter when the DOC temperature is 500 °C with respect to 400 °C 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 of the oxidation of organic material already contained in the particulates or an indication of soot 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 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.

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

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

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 (d_{002}) and average thickness of the graphene layer which composed the soot primary particulates. It is shown that the interlayer spacing from the soot produced from RME and butanol blends combustion is smaller than those found in the soot produced from diesel combustion (Figure 5). However, there are no statistical significant differences between the average thicknesses of the graphene layer derived from the combustion of the studied 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 shows that the DOC does not produce any statistical significant effect to the microstructural parameters obtained from the PM of all the fuels.

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.

CO reduction in the DOC

The CO and HCs engine output emissions from the combustion of conventional diesel fuel are higher compared to the rest of the tested fuels (Figure S6 included in supporting information). The high level of CO and HCs for diesel combustion hampers the CO adsorption onto the catalyst (zeolites) at low exhaust gas temperatures.[10] leading to a delay in the start of CO light-off compared to the other fuels (Figure 6). On the contrary, the lower engine output HC and CO concentration from the combustion of RME and alcohol blend (Figure S6 included in supporting information) reduces the possibility for obstruction from CO and HC competition and 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]

Once the oxidation has started, there are some plateaus in the CO light-off curves for most of the fuels (around 100-150 °C). At high exhaust temperatures, CO is not 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), 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 due to high hydrocarbon depletion as shown in Figure 7. At higher temperatures (approximately 180 °C), the CO oxidation in the DOC catalyst for diesel combustion reaches 100 % at lower temperature compares to the rest of the fuels, especially for RME (Figure 6). The exhaust from the RME combustion has the lowest level of CO and the highest levels of NO_x leading to reduced exothermic and increased competition for active sites between CO and NO. [23]

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).

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 hydrocarbons which have been reported to be more difficult to be adsorbed and oxidised.[18, 22, 30, 31] Meanwhile, higher HC conversion in the DOC noted when exhaust gas from the combustion of the RME was used and this is due to the absence of aromatic hydrocarbons in the fuel structure. Moderate HC conversion is obtained when exhaust gas from for the combustion alcohol blends was used and this is due to the large presence of diesel in the fuel blend, partially compensated by the presence of the alcohol.

NO to NO_2 oxidation in the DOC

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 NO_2 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 NO_2 production occupying the catalyst active sites as well as the consumption of any NO_2 created by reaction with CO and HCs to form CO_2.

It is noticeable the higher NO_2 concentration downstream the catalyst at temperatures below 350 ˚C was seen in the case of butanol combustion. The formation of some very active oxygenated hydrocarbon components which could be formed in the catalyst can enhance NO_2 production. A similar effect has been already reported in the case of Ag/Al_2O_3 catalyst where the formation of NO_2 is highly promoted under the addition of alcohol fuels.[32,33] At temperatures higher than 350 °C the NO_2 production is not further increasing forming a plateau as the NO_2 production from NO oxidation is thermodynamic limited.[34]

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 being detrimental 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.

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ASSOCIATED CONTENT

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 S1 shows the engine specifications. This information is available free of charge via the Internet at http://pubs.acs.org.

ABBREVIATIONS

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

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Tables Caption

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

Table 1.

Properties	ULSD 100%	RME 100%	Butanol	B16R15D (butanol blend)
Chemical formula	$C_{14}H_{26.1}$	$C_{19}H_{35.3}O_2$	C_4H_9OH	$C_{11}H_{21.4}O_{0.5}$
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 (^oC)	-	-	117.5	
50% distillation (^oC)	264	335	117	
90% distillation (^oC)	329	342	117	

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 NO_2 catalyst outlet concentration from engine operation.

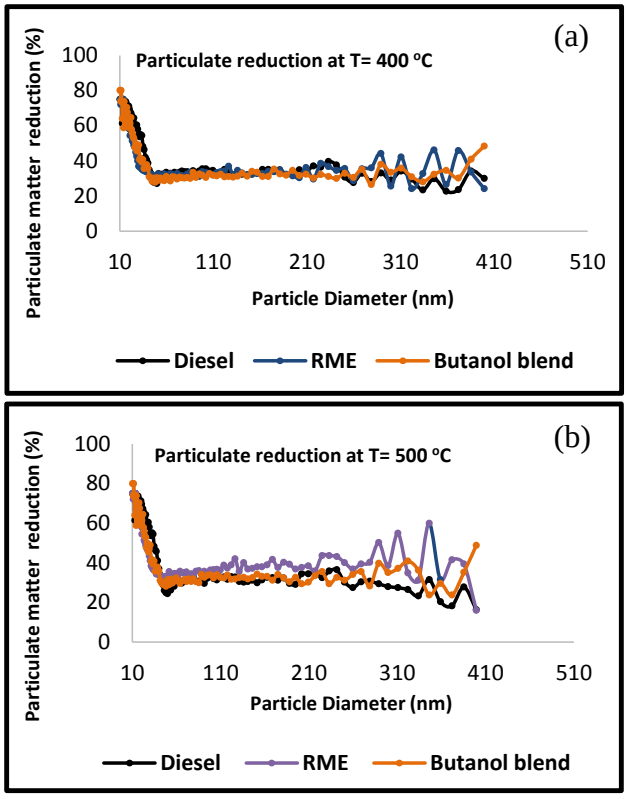
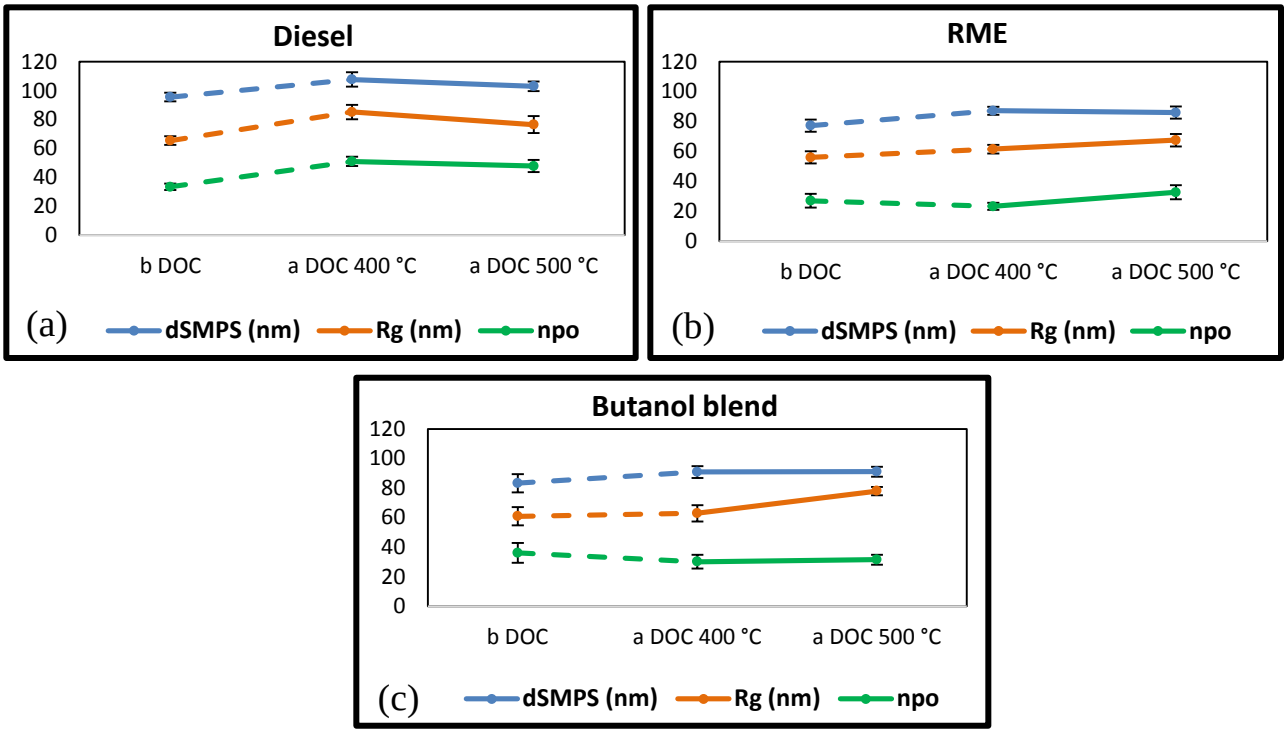
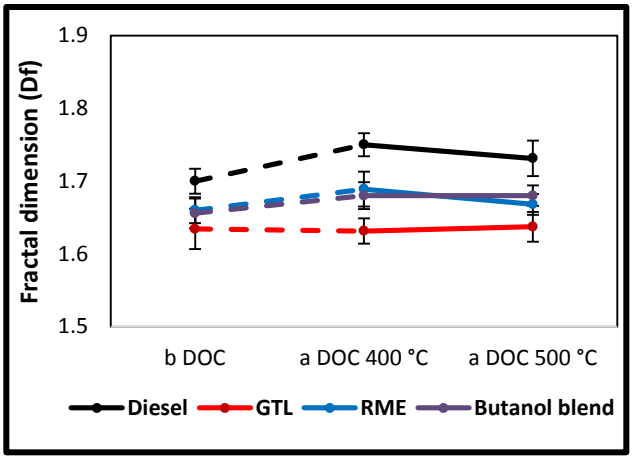

(a)
Particulate reduction at T= 400 °C
Particulate matter reduction (%)
100
80
60
40
20
0
10
110
210
310
410
510
Particle Diameter (nm)
Diesel
RME
Butanol blend
(b)
Particulate reduction at T= 500 °C
Particulate matter reduction (%)
100
80
60
40
20
0
10
110
210
310
410
510
Particle Diameter (nm)
Diesel
RME
Butanol blend

Figure 1.



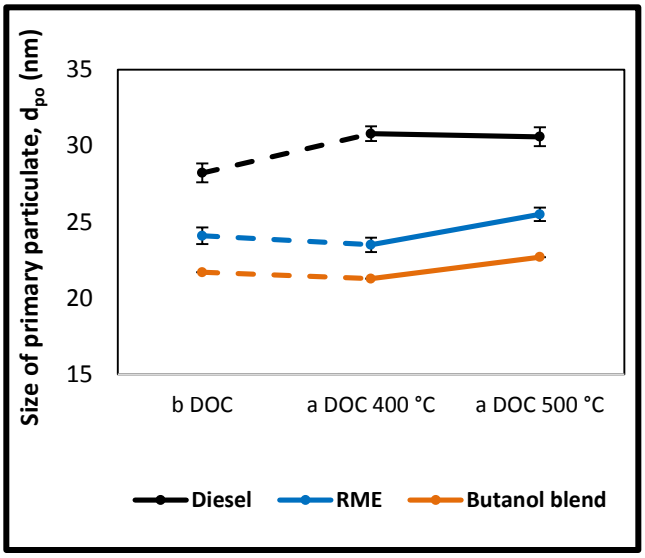
a DOC: after DOC, b DOC: before DOC

Figure 2.



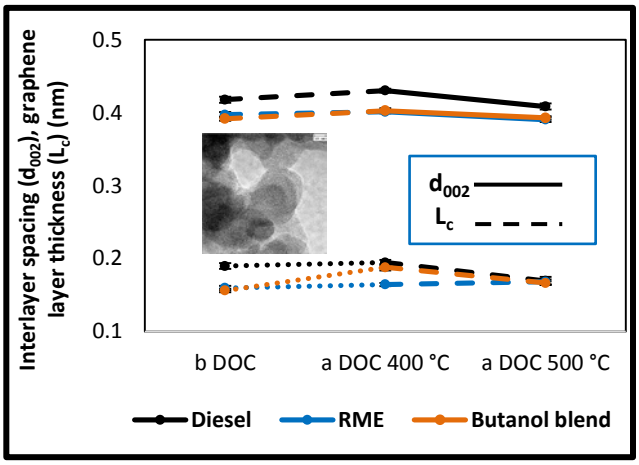
a DOC: after DOC, b DOC: before DOC

Figure 3.



a DOC: after DOC, b DOC: before DOC

Figure 4.



a DOC: after DOC, b DOC: before DOC

Figure 5.

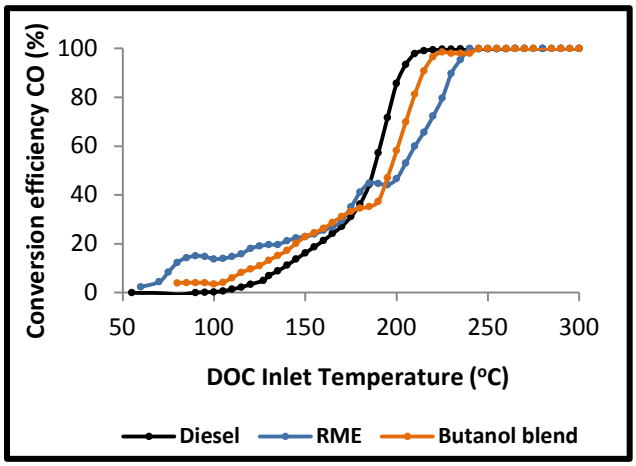

Conversion efficiency CO (%)
100
80
60
40
20
0
50
100
150
200
250
300
DOC Inlet Temperature (°C)
Diesel
RME
Butanol blend

Figure 6.

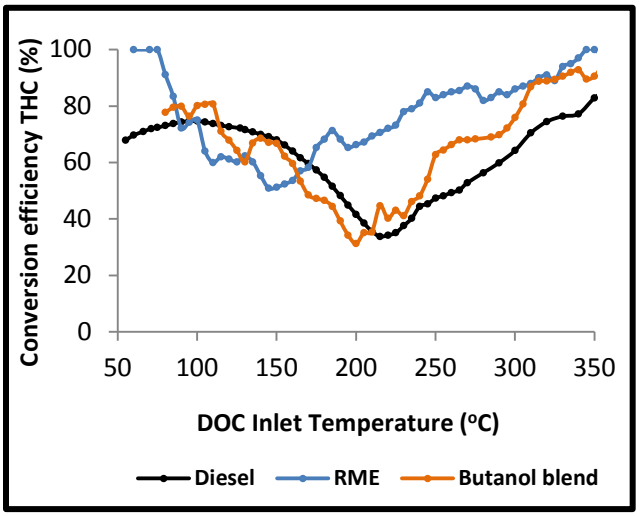

Conversion efficiency THC (%)
100
80
60
40
20
0
50
100
150
200
250
300
350
DOC Inlet Temperature (°C)
Diesel
RME
Butanol blend

Figure 7.

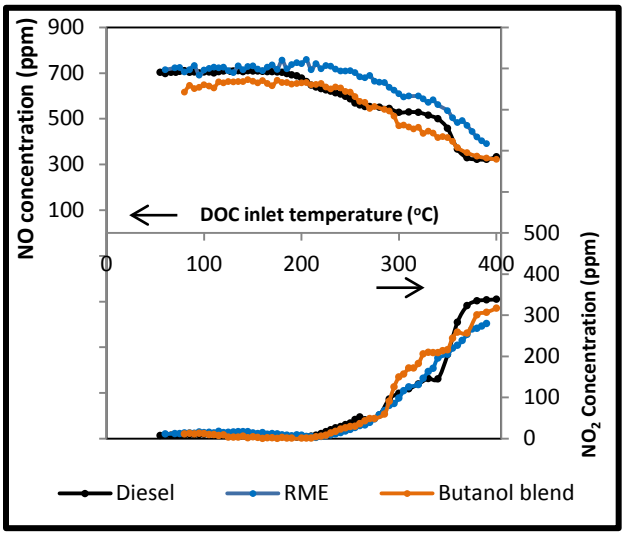

NO concentration (ppm)
900
700
500
300
100
DOC inlet temperature (°C)
0
100
200
300
400
500
400
300
200
100
0
NO2 Concentration (ppm)
Diesel
RME
Butanol blend

Figure 8.

TOC/Abstract art