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Effectiveness of non-noble metal based diesel oxidation catalysts on particle number emissions from diesel and biodiesel exhaust

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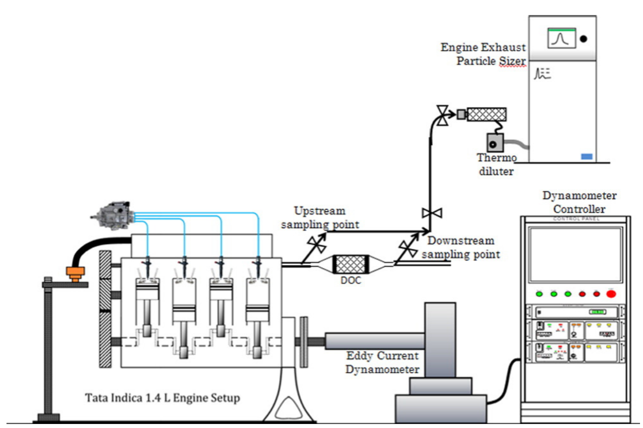
HIGHLIGHTS

- Two non-noble metal catalyzed DOCs were prepared.
- New DOCs were effective in reducing particle number emissions.
- Biodiesel emitted higher particle numbers than diesel downstream of new DOCs.
- CMD shifted towards lower particle sizes for new DOCs with diesel.
- No significant change in CMD of particulate from KB20.

GRAPHICAL ABSTRACT



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ABSTRACT

Two new formulations of non-noble metal based diesel oxidation catalysts based on Co—Ce based mixed oxide (DOC_2) and perovskite catalysts (DOC_3) were prepared and retrofitted in a 4-cylinder diesel engine fueled by diesel and Karanja biodiesel blend (KB20). In this study, their effectiveness in reducing raw exhaust particulate emissions vis-à-vis a commercial diesel oxidation catalyst (DOC_1) was evaluated. Emission characteristics such as particle number-size distribution, mass-size distribution, and surface area-size distribution, total particle number concentration and count mean diameter as a function of engine load at constant engine speed were evaluated. Variations in total particle number concentration as a function of engine speed were also determined. The prepared DOCs and the commercial DOC showed varying degrees of performance as a function of engine operating conditions. Overall, effectiveness of the prepared DOC's appeared to be more fuel specific. For diesel exhaust, overall performance of DOC_1 was more effective compared to both prepared DOCs, with DOC_2 being superior to DOC_3. In case of KB20 exhaust, the overall performance of DOC_2 was either more effective or nearly comparable to DOC_1, while DOC_3 being not so effective. This showed that the DOCs based on Co—Ce based mixed oxide catalysts have potential to replace commercial noble metal based DOC's, especially in engines fueled by biodiesel.

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1. Introduction

In recent decades, diesel engines have become the most important power producing units in the transportation sector. Higher particulate emissions is the main environmental and health concern from these diesel engines, although these are more efficient compared to gasoline engines. At present, most global emission legislations are based on particulate mass measurements. Several studies in open literature (Burtscher 2005; Kittelson 1998; Tan et al., 2014; Zheng et al., 2011) emphasized that particle number emissions should also be a major criterion for future emission regulations. One characteristic of diesel engine exhaust particles that makes it different from particulate generated by other combustion sources, is emission of nano-particles (Kittelson 1998). Adverse health effects due to particulate are far more severe for smaller nuclei mode particulate because of their ability to penetrate deeper into lungs (Agarwal et al., 2013). Diesel engines emit particles in range of 3–300 nm, which can be easily inhaled into the human body through the lungs. Nano-particles are normally considered as particles in the size range of 1–100 nm. Nano-particles comprise of a significant portion of total particles emitted by diesel engines. Nano-particles are not formed during in-cylinder combustion process, but in later stages, when exhaust cools down and gets diluted, causing gas-to-particle conversion. Higher concentration of particles leads to higher surface area availability, providing greater adsorption area for condensation of heavier hydrocarbons. Diesel nanoparticles have been declared as 'carcinogenic' by WHO.

Alternative fuels such as biodiesel are emerging fast therefore they also need to be investigated for utilization in diesel engines. Due to scarcity of petroleum fuels, biodiesel has potential to partially replace diesel and this is being explored worldwide. Hence, it is important to characterize particles emitted by biodiesel for its potential environmental and health compatibility. Some studies have reported particle number emissions from diesel engines fuelled by biodiesel blends and baseline mineral diesel (Agarwal et al., 2011; Jung et al., 2006; Kawano et al., 2006; Puzun et al., 2011). Puzun et al. 2011 investigated particle numbers emitted by a common rail direct injection (CRDI) system equipped diesel engine fuelled with rapeseed biodiesel blends and mineral diesel. It was observed that particles emitted were below 300 nm in size. Biodiesel exhibited bimodal particle number-size distribution with higher particle number concentration of nano-particle size range. Another study showed higher particle number emissions, when an engine was fueled by B100 compared to mineral diesel. Comparable particle numbers were observed when the engine was fueled by KB20 (Agarwal et al., 2011). Jung et al. 2006 reported significant reduction in particle number emissions from a diesel engine fueled by soy biodiesel compared to mineral diesel. Reductions of 38% and 82% in accumulation mode particle numbers and particle volume respectively were obtained. Most nano-particles are composed of organic compounds, formed due to incomplete/partial combustion in the combustion chamber.

Diesel oxidation catalyst (DOC) is a device, which effectively reduces organic fraction of particulates (Johnson and Kittelson 1996). Noble metals like Pt, Pd are used as catalysts for such after treatment devices, which makes them expensive. Some of the transition state metal and perovskite based catalysts have exhibited good potential for application in DOC. Non-noble metal based catalysts have not been investigated extensively for application in DOC however some studies in literature showed their potential applications for oxidation of soot and regulated exhaust gases (Eyssler et al., 2012; Fino et al., 2003; He et al., 2001; Jarrige et al., 2015; Li et al., 2011; Masuda et al., 1998; Song et al., 1997; Teraoka et al., 1996; Yuan et al., 1994). Re_2O_7, MoO_3 and V_2O_5 showed higher catalytic activity compared to higher melting point catalysts such as Fe_2O_4 and Co_3O_4 for carbon black oxidation under NO_2 environment (Liu et al., 2002). MoO_3 and V_2O_5 were also investigated on different support materials. MoO_3/SiC exhibited the best performance (Liu et al., 2002). Kim et al. (2003) investigated the effect of V_2O_5 on the catalytic activity of Pt-based DOC for SO_2 oxidation suppression. Catalytic activity of ABO_3 and K_2NiF_4 (A_2BO_4) catalysts were investigated for simultaneous removal of soot and NOx (Teraoka et al., 1996). It was opined that appropriate substitution of 'K' in the site 'A' of perovskite resulted in superior performance for simultaneous reduction of soot and NOx. He et al., 2001 investigated perovskite type oxides $La_{(1-x)}Sr_xMO_3(M = Co_{0.77}Bi_{0.2}Pd_{0.03})$ for three-way

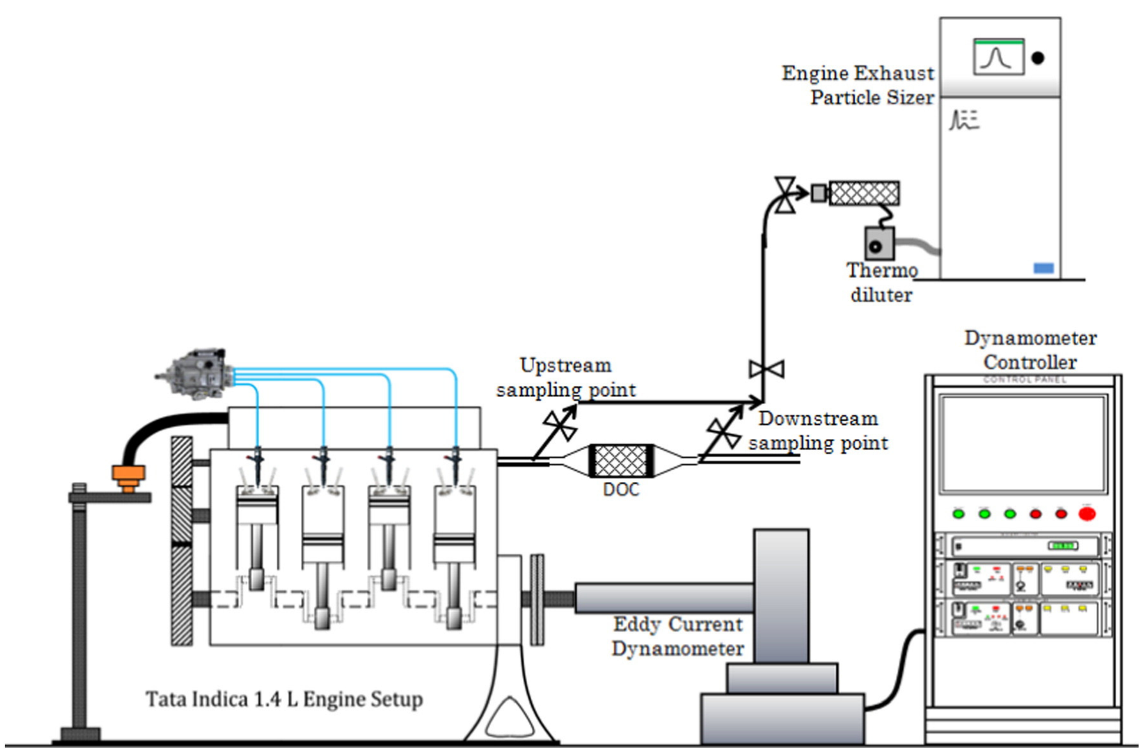

Fig. 1. Schematic of the engine experimental setup.

Table 1
Technical specifications of the test engine.

Make/model	Tata motors/Indica 475
Engine type	Water cooled, compression ignition engine
No. of cylinders	4, inline
Bore/stroke	75 mm/79.5 mm
Cubic capacity	1405 cm^3
Maximum power output	39 kW @ 5000 rpm
Maximum torque	85 Nm @ 2500 rpm
Compression ratio	22:1
Fuel injection system	Rotary pump with electric stop solenoid

catalytic performance. A decreasing order of activity for C_3H_6 elimination: $La_{0.2}Sr_{0.8}MO_3 > La_{0.8}Sr_{0.2}MO_3 > La_{0.4}Sr_{0.6}MO_3 > La_{0.6}Sr_{0.4}MO_3 > LaMO_3$ and a decreasing order of activity for CO oxidation, $La_{0.8}Sr_{0.2}MO_3 > La_{0.2}Sr_{0.8}MO_3 > La_{0.4}Sr_{0.6}MO_3 > La_{0.6}Sr_{0.4}MO_3 > LaMO_3$ were obtained. In the present study, two non-noble metal based DOCs were prepared, retrofitted and investigated for their performance in reduction of particle numbers in the engine exhaust using Karanja biodiesel blend (KB20) vis-à-vis baseline mineral diesel and the results were compared with the commercial DOC.

2. Experimental

2.1. Engine setup

A four cylinder diesel engine (Tata Motors; Indica 475) was used for experimental investigations of the DOCs. Engine was equipped with a rotary fuel injection pump having electric stop solenoid, which facilitated fuel injection. Engine was provided with an EGR system which optimized the emission characteristics of the engine by reducing NOx emission. For the cooling of the engine, a water supply line was connected. Cooling water supply was maintained at a constant flow rate of 480 LPM and the water temperature was maintained at ~25 °C for all operating conditions. Fig. 1 and Table 1 show schematic of the experimental setup and specifications of the test engine, respectively.

Test engine was coupled to an eddy current dynamometer and a dynamometer controller, which was used for loading and unloading the engine. Eddy current dynamometers are electromagnetic loading devices. The engine being tested spins a disk in the dynamometer. Electrical current passes through coils surrounding the disk, which induces a magnetic resistance to the motion of disk. Varying the current varies the load on the engine. Experiments were performed using diesel and 20% (v/v) Karanja biodiesel blend (KB20) at different engine loads at rated engine speed (2500 rpm). To begin with, the engine was equipped with a commercial DOC (BASF) for baseline experiments, followed by experiments with two newly developed non-noble metal catalyzed DOCs. Emissions were measured both upstream and downstream of DOCs. The design of the canister and physical structural configuration of DOCs were same for the tested DOCs. Ceramic substrates used in the study were flow through honeycomb monoliths and the pressure drop across the DOC was ~40 Pa, which is negligible and will be ignored in the experimental investigations. This pressure drop was observed to be the same at all test conditions for all DOCs.

Table 2
Experimental matrix for DOC evaluation at 2500 rpm.

Engine load (%)	Diesel without DOC	KB20 without DOC	Diesel with DOC	KB20 with DOC
0%	√	√	√	√
25%	√	√	√	√
50%	√	√	√	√
75%	√	√	√	√
100%	√	√	√	√

Table 3
Important test fuel properties.

Property	Diesel	KB20
Specific gravity	0.846	0.848
Kinematic viscosity (cSt) @ 40 °C	2.60	3.39
Calorific value (MJ/kg)	42.21	41.42
Flash point (°C)	52.0	79.0

Table 2 shows the experimental matrix. Measured fuel properties namely calorific value, viscosity and density of diesel and KB20 are given in Table 3.

Size-number distribution of particulate emissions was characterized by an Engine Exhaust Particle Sizer™ spectrometer (EEPS) (TSI Inc.; 3090). The EEPS provides both high temporal resolution and reasonable size resolution using the same basic technique as that of a scanning mobility particle sizer (SMPS) system but with multiple detectors working in parallel. EEPS is designed specifically to measure PM emitted from engines and vehicles. It measures particle sizes ranging from 5.6 to 560 nm with a size resolution of 16 channels per decade (a total of 32 channels) up to a maximum concentration of 10^8 particles/cm^3 of the engine exhaust. Number concentration of particulate in the engine out exhaust is higher than the maximum measuring range of the EEPS, hence the exhaust was diluted 560 times prior to measurements, using a rotating disk thermo-diluter (Matter Engineering; MD19-2E). Concentration of particulate was measured in the diluted exhaust and concentration in the actual exhaust was calculated by multiplying the measured values with dilution factor.

2.2. Preparation of DOCs

Cylindrical substrates were chosen in this study because of ease of their retrofitment in the exhaust tail-pipe. Specifications of the ceramic substrates procured from Corning Inc. for this experiment are given in Table 4.

Support and catalyst coatings are important processes in preparing DOCs. The two DOCs evaluated in this study were prepared at NEERI, Nagpur, India using different compositions of non-noble metal catalysts namely (i) Co_3O_4—CeO_2 transition state metal catalyst and (ii) Lanthanum-Manganese based perovskite catalyst ($LaMnO_3$). Preparation of the DOCs was done by following certain steps which are explained in detail in our previous publication (Shukla et al., 2016). For simplicity of explanation, nomenclature used for identification of the test DOCs is given in Table 5.

3. Results and discussion

The prepared DOCs, in comparison to commercial DOC, were evaluated for their effectiveness in reducing particulate emissions in the exhaust of the engine fueled by diesel and Karanja biodiesel blend (KB20). Regulated gaseous emission characterization were also performed for these DOCs, and the results are reported in detail in a previous publication from our group (Shukla et al., 2016). Detailed results related to particulate characterisation are included in this manuscript.

Table 4
Specifications of ceramic DOC substrate.

Make	Corning Inc.
Material	Cordierite
Cell density	400 cpsi/6 mil
Shape	Cylindrical
Diameter/length	143.8 mm/127 mm

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Table 5
Nomenclature used for DOCs.

Diesel oxidation catalyst	Nomenclature
Commercial DOC	DOC_1
Co_3O_4—CeO_2 mixed oxide based DOC	DOC_2
(1) CeO_2 as support	
(2) Co_3O_4—CeO_2 mixed oxide catalyst	
(3) Pd promoter	
$LaMnO_3$ perovskite based DOC	DOC_3
(1) CeO_2 as support	
(2) $LaMnO_3$ perovskite catalyst	
(3) Pd promoter	

3.1. Particle number-size distribution

Fig. 2 shows the particle number-size distribution from mineral diesel and KB20 fuelled engine's exhaust upstream (raw) and downstream of DOC_1, DOC_2, and DOC_3 as a function of engine load (no load to full load) at 2500 rpm. Particle number emissions in raw exhaust were high at no load, which increased at 25% engine load. At low engine loads (no load and 25% load), exhaust temperature was relatively low, which led to particulate formation due to higher degree of incomplete combustion. However, particulate formation decreased at intermediate engine loads and then increased slightly at higher engine loads (75 and 100% load). At 50% engine load, exhaust gas temperature attained a certain level, at which particulate oxidation occurred, leading to reduction in particle numbers. As engine load increased, fuel injection quantity in the combustion chamber also increased, which led to reduction in relative air-fuel ratio (λ).

Lower λ increased the degree of incomplete combustion, which in turn increased particle numbers at higher engine load. Similar trend was also observed for KB20. However, KB20 showed slightly lower particle numbers compared to diesel at identical engine loads. It has been reported that use of biodiesel leads to slightly higher particulate oxidation. Kawano et al. 2006 reported that particulate number-size distribution of diesel and RME was uni-modal and this distribution mostly covered accumulation mode particles at all engine loads. Size distribution of accumulation mode particles of RME shifted towards smaller sizes compared to diesel and peak particle number-size distribution was almost constant at varying engine loads. An increase in engine load increased peak particle number concentration for diesel but reduced the peak particle number concentration for RME. These findings were in agreement with other studies, suggesting that biodiesel particulate mostly comprised of organic matter, which was destroyed inside the combustion chamber at high temperature conditions, typically

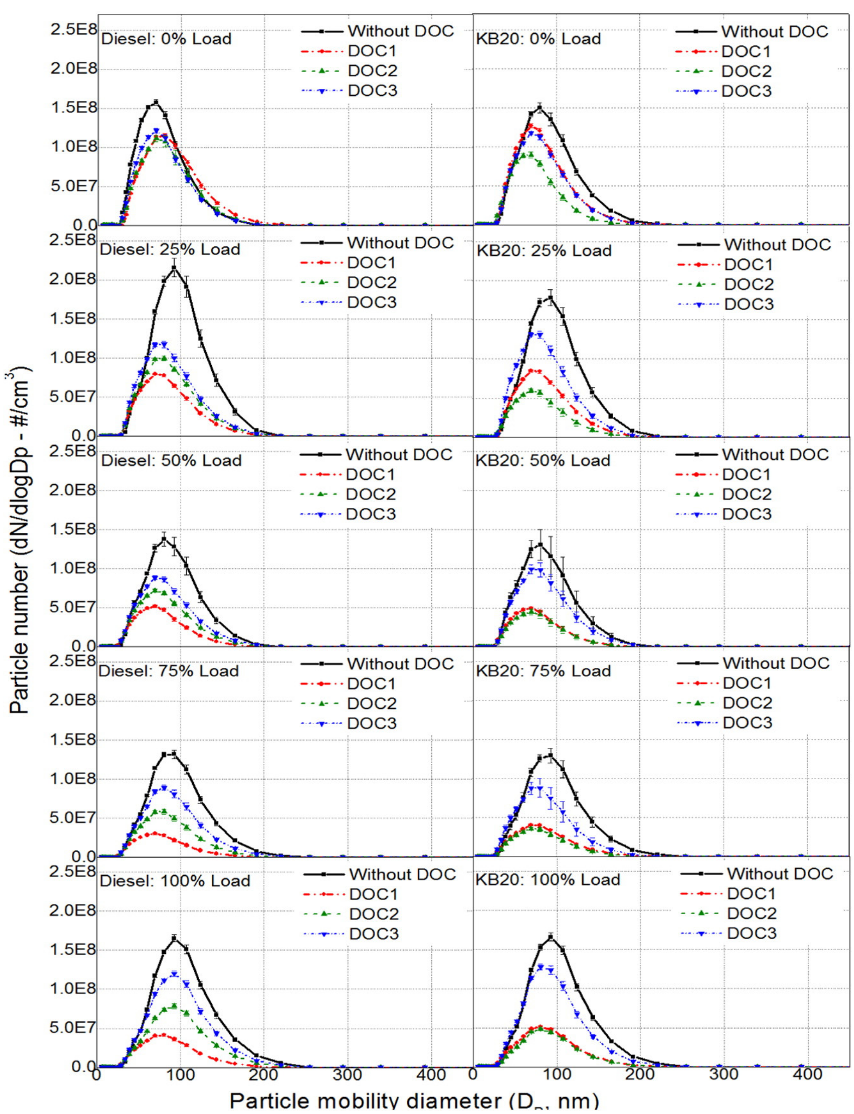

Fig. 2. Effectiveness of DOCs in reducing particle number-size distributions in diesel and KB20 exhaust at 2500 rpm.

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prevailing at higher engine loads. As far as the DOCs are concerned, their effectiveness in reducing particle number-size distributions increased at higher engine loads. It can be observed that DOC_1, DOC_2 and DOC_3 were not effective at no load for both test fuels, diesel and KB20. However, their effectiveness improved with increasing engine loads. This was primarily because of increase in exhaust gas temperature with increasing engine load. Elevated exhaust gas temperature is suitable for optimum activity of catalyst present in DOCs. For diesel exhaust, DOC_1 showed higher reduction in particle numbers and was the most effective DOC at higher engine loads. Effectiveness of DOC_2 and DOC_3 for particle number reduction was also good at intermediate and high engine loads. For KB20 exhaust, DOC_1 and DOC_2 gave superior and near comparable performance in terms of particle number distribution reduction (Fig. 2). This indicated that DOC_2 is effective in reducing particle number distribution in the exhaust of KB20. The efficiency of PM reduction by both DOCs increased with increasing engine load due to elevated exhaust gas temperature, which favored higher degree of soot oxidation. Studies have shown that diesel and KB20 particulate have different characteristics (Agarwal et al., 2015). The interaction of Co_3O_4-CeO_2 mixed oxide catalyst with biodiesel particulate favor their higher oxidation. Some specific characteristics of biodiesel particulate such as presence of oxygenated unburnt hydrocarbons, oxygen content etc. contribute to superior performance of DOC_2. Agarwal et al. 2015 reported that particle number emissions for B100 were higher than baseline mineral diesel. However, these were comparable for diesel and KB20 at lower loads. Jung et al. 2006 investigated the effect of biodiesel on oxidation of particulate using soy methyl ester (SME) and diesel at 1400 rpm engine speed and 75% load. Accumulation mode particle number concentration and particle volume distribution for SME were found to be lower by 38 and 82%, respectively. It was also reported that lower particle numbers existed for SME compared to mineral diesel (for particle size range above 50 nm). However, number concentrations were observed to be similar for nuclei mode particles below 50 nm. This indicated lower particle mass for KB20 because of relatively lower soot pyrolysis, primarily due to presence of oxygen in the test fuel. Higher number of engine out nuclei mode particles for KB20 was due to presence of large number of condensed droplets of high boiling point hydrocarbons in the test fuel.

3.2. Particle surface area-size distribution

Fig. 3 shows particle surface area-size distribution for tested DOCs, which shows similar trend as observed for particle number-size distribution curves.

Particulate surface area is very important from toxicity point of view because it provides potential sites for adsorption of toxic, high boiling point organic compounds in vapor phase, which are present in the

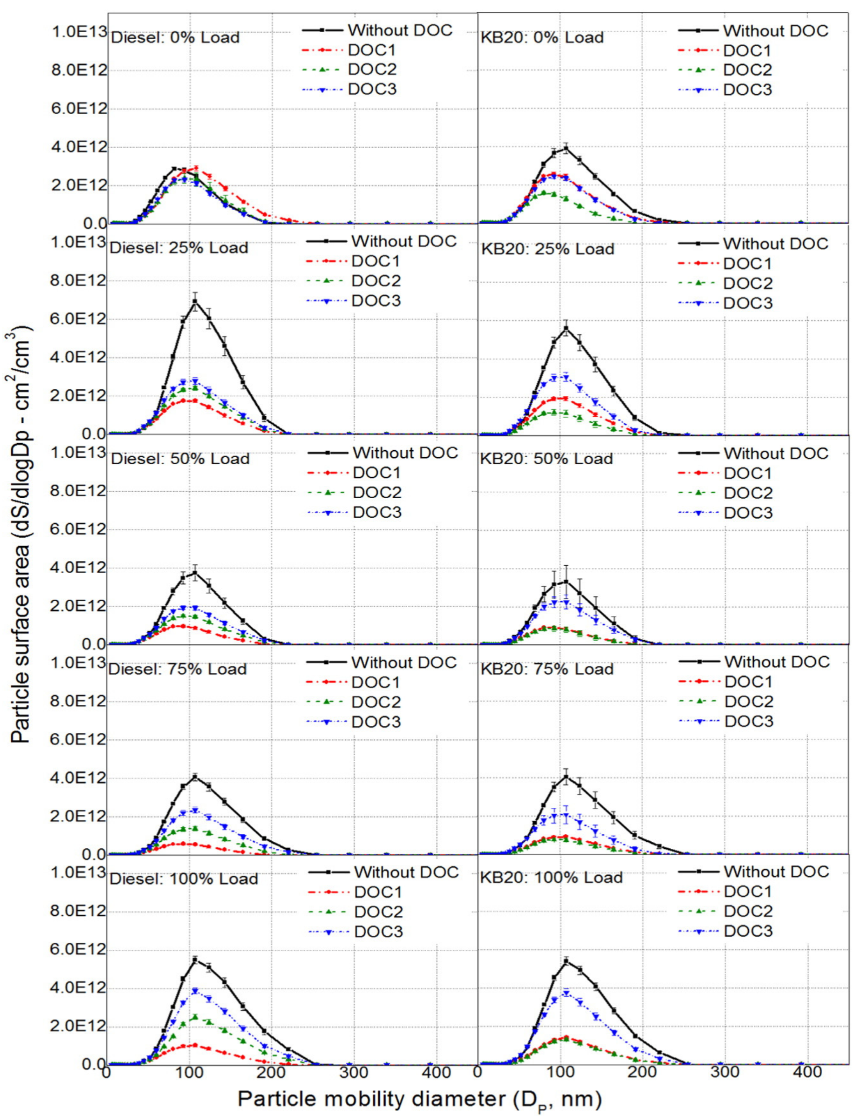

Fig. 3. Effectiveness of DOCs in reducing particle surface area-size distribution in diesel and KB20 exhaust at 2500 rpm.

engine exhaust. With reference to particulate surface area-size distribution, it was observed that peak particle surface area distribution was the lowest at no load and 50% load for raw exhaust (from both diesel and KB20). At 25% engine load, peak particle surface area-size distribution was the highest in the raw exhaust for both test fuels. This is because of slight shifting of peak particle number density towards the right (Fig. 2) for the same operating condition (25% load). DOC_1 was found to be the most effective in particle surface area reduction, followed by DOC_2 and DOC_3 for diesel exhaust. Again, DOC_2 performance was superior compared to DOC_1, when engine was fueled with KB20. Toxicity of particles is considered to be directly associated with particulate surface area availability. Higher particulate surface area provides base for higher condensation of volatile toxic organic compounds present in the engine exhaust. It is therefore desirable to have lower surface area of particles present in the engine exhaust and newly developed DOCs are quite effective in the same.

3.3. Particle mass-size distribution

Fig. 4 shows mass-size distribution of soot particles emitted from the engine tailpipe. It has been widely debated that emission regulations should also consider particle numbers. Diesel engines are infamous for higher nano-particles and fine-particles emissions into the atmosphere. These nano-particles and fine-particles are emitted in large numbers, however their overall contribution to particulate mass is rather negligible (Kittelson 1998). (See Fig. 5.)

In the present study, particle number emissions were higher at 25% engine load compared to no load, in raw engine exhaust (Fig. 2) from both test fuels. It may be noted that particle mass-size distribution was evaluated from the particle number size-distribution by assuming the particles to be perfectly spherical and the particle density to be 1 g/cm^3. Particle mass-size distribution was lower at no load and relatively higher at 25% load (Fig. 4). This was due to higher particle numbers in larger sizes. Larger diameter particles contribute more to the PM mass. Particle mass-size distribution was relatively lower at 50% load due to higher degree of combustion and higher in-cylinder temperature. The test DOCs significantly reduced PM emissions in the engine exhaust. At higher loads, DOC_1 and DOC_2 showed comparable performance in reducing particle mass distribution, when the engine was fueled by KB20.

3.4. Total particle number concentration

Total particle number emission is an important criterion for evaluating effectiveness of the prepared test DOCs. It is desirable to have lower total particle number emissions. Total particle numbers emission limits

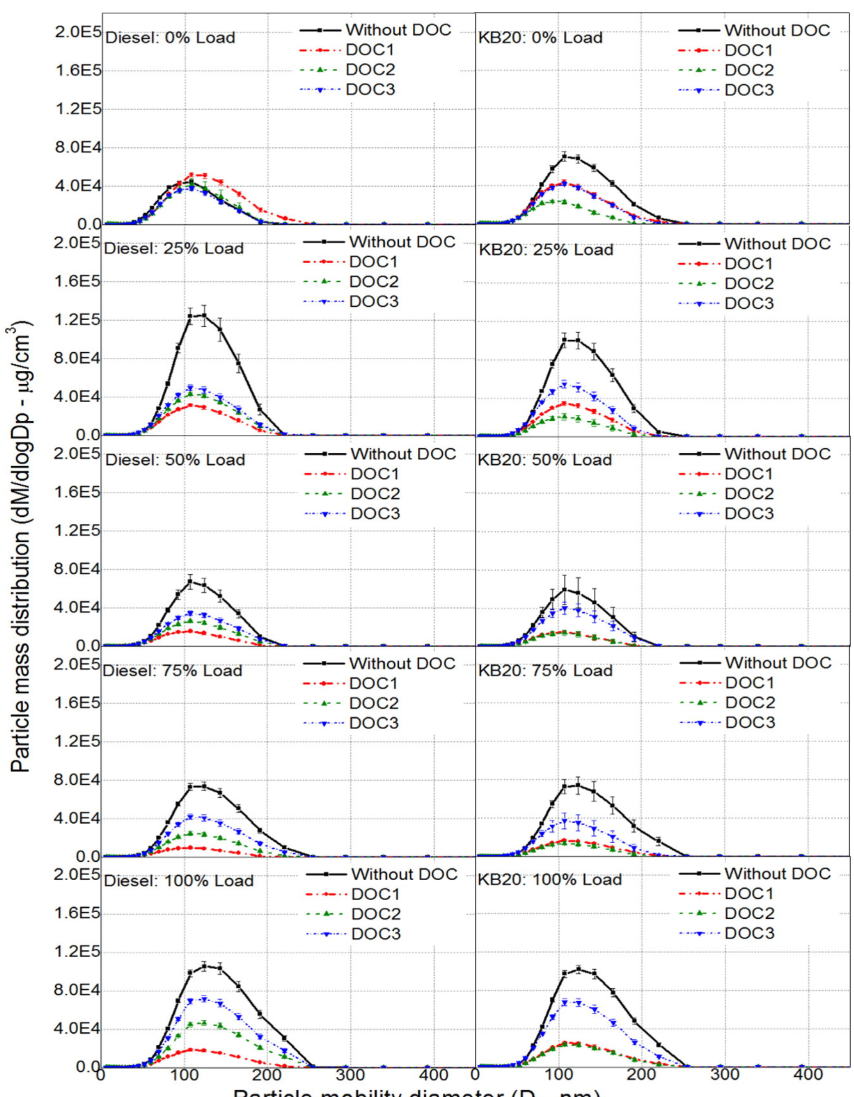

Fig. 4. Effectiveness of DOCs in reducing particle mass -size distribution in diesel and KB20 exhaust at 2500 rpm.

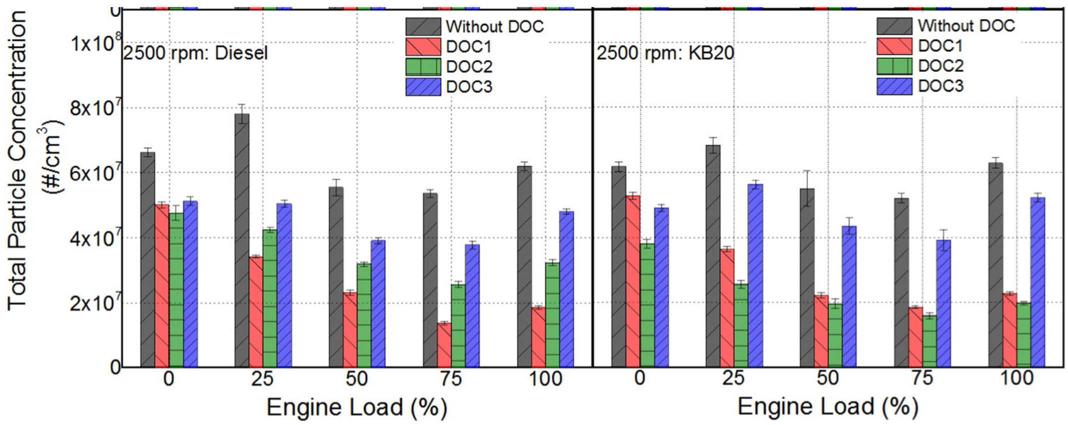

Fig. 5. Effectiveness of DOCs in reducing total particle number concentration in diesel and KB20 exhaust at 2500 rpm.

have already been enforced by contemporary emission legislations in several developed countries of the world. Fig. 6 shows total particle numbers emitted by the engine fueled by diesel and KB20 with and without DOCs. Total particle number concentrations were high, when exhaust was sampled without DOCs. All three DOCs (DOC_1, DOC_2 and DOC_3) were effective in reducing total particle number emissions. Total particle number concentration was the highest at 25% engine load for raw exhaust, which decreased with increasing load but again slightly increased at full load. This trend was identical for both test fuels.

It was observed that DOCs significantly reduced total particle number concentrations and their effectiveness increased with increasing engine load. At higher engine load, greater fuel quantity was injected, which led to higher in-cylinder temperature. Higher in-cylinder temperature resulted in higher exhaust gas temperature, which was suitable for higher oxidation of particulate that pass through these DOCs. KB20 showed slightly lower total particle number concentrations, when exhaust samples were analyzed without DOC. DOC_1 was found to be the most effective in reducing diesel exhaust particles whereas DOC_2 showed promising results in reducing KB20 exhaust particles with performance slightly superior to DOC_1. Performance of DOC_3 was inferior to DOC_1 and DOC_2. Support material in DOC_2 was CeO_2, which has very good oxygen adhesion, retention and release characteristics (Kirchnerova et al., 2002). These properties of support material provide adequate oxygen for oxidation and enhanced catalytic activity in this DOC.

It has been observed that better atomization characteristics of fuel in the combustion chamber result in lower particulate mass emission. However, some previous studies have shown that superior fuel atomization increases particle number emissions despite of lower particle mass emissions. Particle number emissions are mainly affected by fuel atomization characteristics in the combustion chamber. Higher viscosity and density of biodiesel results in formation of relatively larger spray droplets, which lead to formation of lower number of particulate. These are further reduced by DOCs in the present study. However, inherent oxygen content of biodiesel enhances fuel reactivity, which results in reduced particle mass emissions, as explained in our previous publication (Shukla et al., 2016).

3.4.1. Variation in total particle number concentration with engine speed

Variations in total particle number concentrations were evaluated both upstream and downstream of the DOCs as a function of engine load and speed, in order to assess their performance. Figs. 6 shows colored contour graphs, wherein particle number concentrations can be differentiated by different colors representing a range of particle number concentrations (10^7 to 8×10^7 particles/cm^3 corresponding to bright red to violet). For raw exhaust (upstream of DOCs; top two graphs), significantly higher particle number concentrations were observed for most engine operating conditions. Lowest concentrations were observed at intermediate loads and lower engine speeds.

Particle number emissions downstream of DOCs showed significant reduction, which are indicated by bright red and yellow contours. DOC_1 showed higher reduction in total particle number concentration, compared to DOC_2 for diesel with varying load and speed (Fig. 6). However, DOC_2 showed comparable reduction, when the engine was fueled by KB20. Performance of DOC_1 was not very effective at no load condition for the speed range tested.

Catalytic properties of DOC_2 were favorable for oxidation of KB20 particulates. This indicated that KB20 particulate have certain peculiar characteristics, which were utilized by DOC_2. DOC_3 also reduced particle

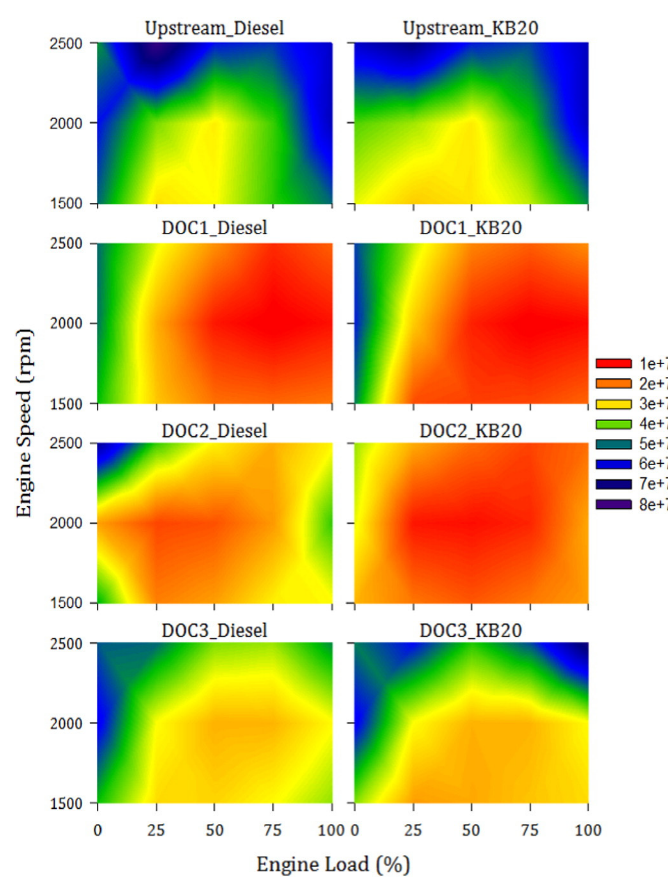

Fig. 6. Variations in total particle number concentration with engine speed for different test DOC's upstream (top two) and downstream (bottom six) for diesel and KB20.

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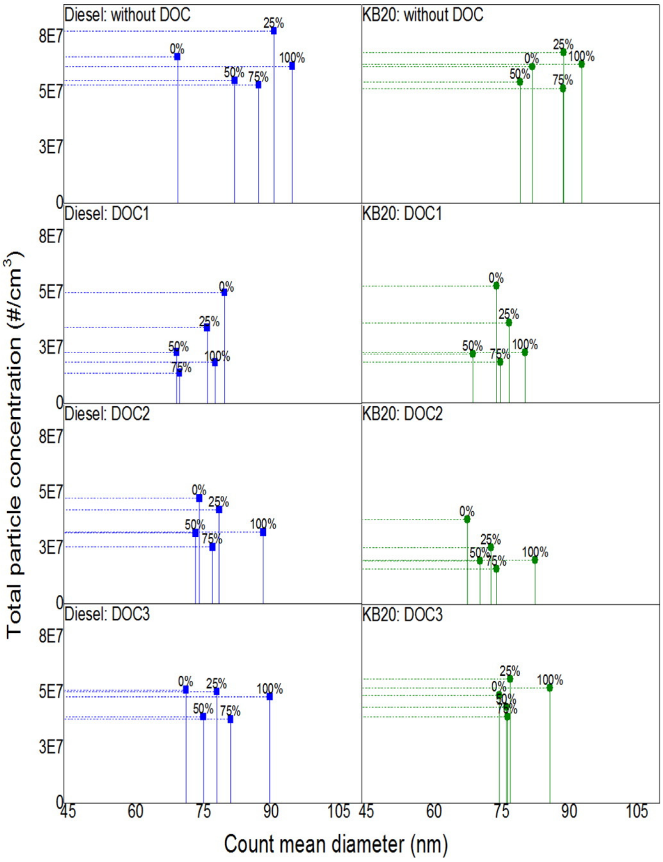

Fig. 7. Effect of DOCs on count mean diameter vs. total particle number concentration emitted by diesel and KB20 at 2500 rpm (*Note:* % inside each figure refers to engine load).

number emissions effectively, but not as efficiently as DOC_2. This indicated that the catalyst used in DOC_2 was superior to that used in DOC_3.

3.5. Count mean diameter (CMD)

For comparison of mean diameter of particulate emitted by the engine fueled by mineral diesel and KB20, with and without DOC, count mean diameter (CMD) was calculated at 2500 rpm engine speed. This is a measure of mean diameter of particles emitted by an engine, which provides valuable information about average particle size at a particular engine operating condition. It is important to evaluate the relationship between total particle number concentration and CMD as it is not desirable to have higher number of particles with smaller sizes, which can easily penetrate deeper into human lungs. Following equation was used for calculating CMD at each engine operating condition:

$$CMD = \frac{n_1 d_1 + n_2 d_2 + n_3 d_3 + \ldots\ldots + n_n d_n}{n_1 + n_2 + n_3 + \ldots\ldots + n_n} \qquad (1)$$

Here, n_i is particle number concentration corresponding to diameter d_i.

Fig. 7 shows that CMD was maximum at 100% load for both diesel and KB20. This indicated that higher engine load resulted in emission of overall larger particles. Remarkably, 25% load (diesel and KB20) showed highest particle number concentration as well as higher CMD, which was almost similar to that at 100% load. Particle number concentrations were drastically reduced by DOC_1 and DOC_2. CMD shifted towards lower size range at most operating conditions. Reduction in total particle number concentration in exhaust is favorable, nonetheless shifting of CMD towards lower sizes is undesirable. Lower CMD indicated higher surface area available per unit mass of particulate for adsorption of high molecular weight hydrocarbons, which are carcinogenic. DOC_3 was also effective in reducing total particle numbers and lowering CMD for all operating conditions. However, CMDs for both test fuels using DOC_3 were relatively larger compared to those obtained by using DOC_2 and DOC_1. For DOC_2, 100% load showed different results and CMD was high (close to ~90 nm) along-with lower particle numbers, which reduced their toxic potential. CMD did not seem to be affected significantly when KB20 was used instead of mineral diesel, however total particle number concentration reduced with use of KB20. Significantly higher particle number emissions were observed at no load, downstream of DOCs (diesel and KB20). This indicated that DOCs were ineffective in oxidizing most particles at no load, primarily due to lower exhaust gas temperatures, resulting in retarded catalytic activity under these conditions. Fig. 8 shows the brake specific fuel consumption (BSFC) for diesel and KB20 at 2500 rpm at various engine loads. It can be seen that BSFC reduces with increasing engine load.

4. Conclusions

Two new DOC based on non-noble metals were developed and used in engine experiments for reducing exhaust particles from Karanja Biodiesel blend (KB20) and baseline diesel and their performance was compared with commercial DOC. Emission characteristics evaluated included particle number-size distribution, mass-size distribution, and surface area-size distribution, total particle number concentration and count mean diameter as a function of engine load at constant engine speed. Variations in total particle number concentrations as a function of engine speed were also determined. Exhaust of KB20 showed slightly reduced emission of total number of particles compared to diesel. In diesel exhaust, DOC_1 showed maximum effectiveness in reducing maximum particle number concentration. DOC_2 and DOC_3 showed nearly comparable performance at intermediate and higher engine loads. Overall comparison of DOC_2 and DOC_3 showed that DOC_2 was more effective in reducing emission of total particle numbers at all test conditions for both diesel and KB20. It may be noted that particle number-size distribution for exhaust sampled downstream of DOC_2 was nearly comparable to that of DOC_1 at 50% and higher loads, when the engine was fueled by KB20. This indicated that DOC_2 performed satisfactory in oxidation of exhaust particulate. Support material in DOC_2 was CeO_2, which showed excellent oxygen adhesion, retention and release. These properties ensured availability of oxygen for oxidation and enhanced activity of catalyst present in DOC_2. Good performance of DOC_2 for exhaust of KB20 can also be seen from reduction in total particle number concentration. Variations in total particle number

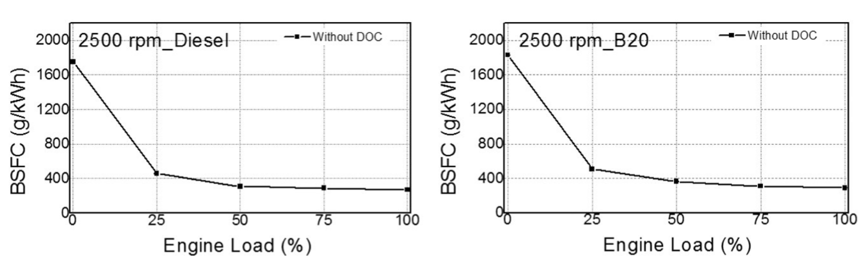

Fig. 8. BSFC for diesel and KB20 at different engine loads.

concentration were evaluated at varying engine speed and load. DOC_2 used for exhaust of KB20 yielded significant reduction in total particle number emissions at tested engine loads and speeds. Reduction in total number concentration of particles in exhaust is favorable nonetheless shifting of CMD towards lower size range is undesirable. CMD for DOC_3 was relatively higher compared to DOC_1 and DOC_2 for both test fuels. CMD does not seem to be affected significantly when KB20 was used instead of diesel, yet total particle number concentration reduced with use of KB20. Overall, DOC_2 was as effective as noble metal based commercial DOC in controlling particulate emission from diesel and KB20 fuelled engine.

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References

Agarwal, A.K., Gupta, T., Dixit, N., Shukla, P.C., 2013. Assessment of toxic potential of primary and secondary particulates/aerosols from biodiesel vis-a-vis mineral diesel fuelled engine. Inhal. Toxicol. 25, 325–332.

Agarwal, A.K., Gupta, T., Kothari, A., 2011. Particulate emissions from biodiesel vs diesel fuelled compression ignition engine. Renew. Sust. Energ. Rev. 15, 3278–3300.

Agarwal, A.K., Gupta, T., Shukla, P.C., Dhar, A., 2015. Particulate emissions from biodiesel fuelled CI engines. Energy Convers. Manag. 94, 311–330.

Burtscher, H., 2005. Physical characterization of particulate emissions from diesel engines: a review. J. Aerosol Sci. 36, 896–932.

Eyssler, A., Winkler, A., Safonova, O., Nachtegaal, M., Matam, S.K., Hug, P., et al., 2012. On the state of Pd in perovskite-type oxidation catalysts of composition a (B, Pd) O3 ± δ (A = La, Y; B = Mn, Fe, Co). Chem. Mater. 24, 1864–1875.

Fino, D., Russo, N., Saracco, G., Specchia, V., 2003. The role of suprafacial oxygen in some perovskites for the catalytic combustion of soot. J. Catal. 217, 367–375.

He, H., Dai, H., Au, C., 2001. An investigation on the utilization of perovskite-type oxides La 1− x Sr x MO 3 (M = Co 0.77 Bi 0.20 Pd 0.03) as three-way catalysts. Appl. Catal. B Environ. 33, 65–80.

Jarrige, I., Ishii, K., Matsumura, D., Nishihata, Y., Yoshida, M., Kishi, H., et al., 2015. Toward optimizing the performance of self-regenerating Pt-based perovskite catalysts. ACS Catal. 5, 1112–1118.

Johnson, J.E., Kittelson, D.B., 1996. Deposition, diffusion and adsorption in the diesel oxidation catalyst. Appl. Catal. B Environ. 10, 117–137.

Jung, H., Kittelson, D.B., Zachariah, M.R., 2006. Characteristics of SME biodiesel-fueled diesel particle emissions and the kinetics of oxidation. Environ. Sci. Technol. 40, 4949–4955.

Kawano, D., Ishii, H., Goto, Y., Noda, A., Aoyagi, Y., 2006. Application of biodiesel fuel to modern diesel engine. SAE Technical Paper.

Kirchnerova, J., Alifanti, M., Delmon, B., 2002. Evidence of phase cooperation in the LaCoO 3–CeO 2–Co 3 O 4 catalytic system in relation to activity in methane combustion. Appl. Catal. A Gen. 231, 65–80.

Kittelson, D.B., 1998. Engines and nanoparticles: a review. J. Aerosol Sci. 29, 575–588.

Li, L., Shen, X., Wang, P., Meng, X., Song, F., 2011. Soot capture and combustion for perovskite La–Mn–O based catalysts coated on honeycomb ceramic in practical diesel exhaust. Appl. Surf. Sci. 257, 9519–9524.

Liu, S., Obuchi, A., Uchisawa, J., Nanba, T., Kushiyama, S., 2002. An exploratory study of diesel soot oxidation with NO 2 and O 2 on supported metal oxide catalysts. Appl. Catal. B Environ. 37, 309–319.

Masuda, K., Shinoda, K., Kato, T., Tsujimura, K., 1998. Activity enhancement of Ag/mordenite catalysts by addition of palladium for the removal of nitrogen oxides from diesel engine exhaust gas. Appl. Catal. B Environ. 15, 29–35.

Puzun, A., Wanchen, S., Guoliang, L., Manzhi, T., Chunjie, L., Shibao, C., 2011. Characteristics of particle size distributions about emissions in a common-rail diesel engine with biodiesel blends. Prog. Environ. Sci. 11, 1371–1378.

Shukla, P.C., Gupta, T., Labhsetwar, N.K., Agarwal, A.K., 2016. Development of low cost mixed metal oxide based diesel oxidation catalysts and their comparative performance evaluation. RSC Adv. 6, 55884–55893.

Song, K.-S., Kang, S.-K., Kim, S.D., 1997. Preparation and characterization of Ag/MnOx/perovskite catalysts for CO oxidation. Catal. Lett. 49, 65–68.

Tan, P.-q., S-s, R., Hu, Z.-y., D-m, L., Li, H., 2014. Particle number emissions from a light-duty diesel engine with biodiesel fuels under transient-state operating conditions. Appl. Energy 113, 22–31.

Teraoka, Y., Nakano, K., Shangguan, W., Kagawa, S., 1996. Simultaneous catalytic removal of nitrogen oxides and diesel soot particulate over perovskite-related oxides. Catal. Today 27, 107–113.

Yuan, S., Mériaudeau, P., Perrichon, V., 1994. Catalytic combustion of diesel soot particles on copper catalysts supported on TiO 2. Effect of potassium promoter on the activity. Appl. Catal. B Environ. 3, 319–333.

Zheng, Z., KC, J., Liu, Z., TD, D., Jung, H., S, H., et al., 2011. Measurement of diesel engine emitted nanoparticles. Measurement.

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