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Comparative study of using multi-wall Carbon Nanotube and two different sizes of Cerium Oxide Nanopowders as fuel additives under various diesel engine conditions

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HIGHLIGHTS

- CeO_2 Nano powders and CNT as additives can reduce pollutant emissions
- CeO_2 in smaller size emits higher CO, NO_x and PN but lower HC than the larger size.
- CNT leads to lower gaseous emissions but higher PN emissions than CeO_2
- Comparative tests with and without additives were obtained at various engine conditions.

Abstract

This research reports the study of using Cerium oxide (CeO_2) nano additive with two different sizes (25 nm and 50 nm) blended with standard diesel fuel (DF-Ce25 and DF-Ce50) at various engine speed and load conditions. Moreover, carbon nanotube (CNT) is employed as a single additive (DF-CNT). Results indicate that the in-cylinder pressure of DF-CNT is slightly lower than that of DF under the most conditions due to more heat absorption during the evaporation process. In contrast, the in-cylinder pressure of DF-Ce25 and DF-Ce50 is

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higher than that of DF at relatively low speed due to the improved fuel spray and faster combustion. In terms of emissions, all fuels with nano-additives are overall lower than DF. DF-CNT can reduce CO, HC, NO_x and PN by 20%, 22.6%, 21% and 5.5% respectively compared with DF, due to its improved spray and lower combustion temperature. Meanwhile, DF-Ce25 and DF-Ce50 produce the overall higher level of emissions of CO, NO_x and HC than DF-CNT except for PN. A minimum engine (load-speed) limit and a maximum engine limit are found for CO emissions. Furthermore, DF-Ce25 emits higher NO_x and lower HC than DF-Ce50, because CeO_2 of 25 nm has a higher reaction rate of CeO_2 due to its larger surface area and in return hinders the reaction of Ce_2O_3. The difference of PN emissions between the two sizes of CeO_2 is the comprehensive result of the oxidization of particulate matters and the aggregation of unburnt fuel.

Keywords: Cerium oxide (CeO_2), nanopowder size, carbon nanotube (CNT), pollutant emissions, diesel engine

Nomenclature

BSFC	Brake specific fuel consumption
CeO_2	Cerium oxide nanopowder
CNT	Multi-wall carbon nanotube
CO	Carbon monoxide
DF	Standard diesel fuel
DF-Ce25	DF blended with Cerium oxide nanopowder of 25 nm size
DF-Ce50	DF blended with Cerium oxide nanopowder of 50 nm size
ESC	European Stationary Cycle
HC	Unburnt hydrocarbons
HRR	Heat release rate
LHV	Lower heating value
NO_x	Nitric oxides
PM	Particulate matter
PN	Number concentration of PM

1. Introduction

With the increasing concerns on the environmental problems caused by the emissions from the burning of fossil fuels, ever strict regulations have been released such as the Euro VI to dramatically restrain gaseous pollutants and particulate matters (PM) from the engines [1, 2]. The current mainstream methods to reduce pollutants emitted from the combustion of fossil fuels are by using alternative fuels, conducting fuel modification, retrofitting engine and improving the after treatment technologies [3-5].

It is popular to blend commercial fossil fuels with additives such as alcohols and biofuels. However, most of these additives suffer from the shortcomings such as low energy density, relatively poor physical properties and limited blending ratios etc. [6-8]. Nanofluid is a mixture consisting of nano-sized materials dispersed in a base fluid, which is widely used in different fields [9]. Nowadays, Nanomaterials have been employed as fuel additives to enhance the properties of the original fuels and become effective approaches to improve engine output and reduce emissions [10-12]. Among various nano additives, the metallic or metallic oxide nanomaterials such as Al_2O_3, CuO, ZnO, TiO_2, MnO and Fe_2O_3 are the most popular types and have demonstrated the potential to provide higher power output, higher overall engine thermal efficiency, lower NO_x and HC emissions [10, 11, 13-18].

Cerium oxide (CeO_2) is a newly developed metallic oxide nano additive as reported in the literature below. Zamankhan et al. [19] ran a gasoline engine burning gasoline with CeO_2 nanopowder and found less emissions were produced at high speeds and throttles. Vairamuthu et al. [20] added CeO_2 nanopowder to the biodiesel-diesel blend and tested them in a diesel engine at constant speed and load. Results indicated that the unburnt hydrocarbon

(HC) and NO_x were reduced with improved brake thermal efficiency. Nevertheless, the performance of using CeO_2 as the fuel additive at different speeds and loads were not investigated. The follow-on research reported by Saraee et al. [21], who tested the performance of diesel fuel with Cerium oxide nano additive under three different concentrations at varying engine speed, and found a significant reduction of NO_x and HC but increased CO emissions. However, the impact of load on the performance of CeO_2 nano additive was not considered. In contrast, Aghbashlo et al. [22, 23] emulsified biodiesel-diesel-nano CeO_2 blends with water for engine test at 1000 rpm speed and varying load. It was found that the emulsions with CeO_2 had lower CO, HC and NO_x emissions but increased brake thermal efficiency and normalized exergy destruction. However, these researches did not include the study of particulate matters (PM) emissions with the existence of CeO_2 nano additive. Gross et al. [24] studied the kinetic and reaction mechanism of CeO_2 with emitted PM in a cell. Results indicated that CeO_2 is capable of oxidising PM and its catalysis would be improved with rising temperature. However, this investigation was done in a cell with a constant heating rate rather than in an engine cylinder. Furthermore, the influence of different sizes of nano CeO_2 has been rarely studied in previous research works. In addition, most researches on CeO_2 nano additive introduced in surfactants or emulsified fuels which disturbed results and thus made it difficult to identify the actual influence of CeO_2 on engine performance and emissions.

Carbon nanotubes (CNT) is a nanomaterial widely used in electromagnetism and heat recycling system due to its extraordinary characteristics in electrical conductivity and heat absorption. Recently, some researchers [25-27] attempted to mix CNT with other additives such as Cerium oxide nanopowder, silver nanoparticles and ethanol in engine experiments. Different levels of improvement of engine performance were reported in previous studies. However, most of them employed CNT as a support to accelerate the dispersion of other additives rather than investigating the effects of using CNT as the additive of the fuel. As a result, the effect of CNT on engine performance cannot be identified and recognised. Accordingly, Ghanbari et al. [28] used multi-wall CNT as a single additive in diesel-biodiesel blended fuels and found the blended fuel with CNT has lower brake specific fuel consumption and CO emissions but increased HC emissions than neat diesel fuel. However, this research compared the performance of diesel-biodiesel-CNT blends with neat diesel fuel, so the influence of CNT alone was still unclear. Moreover, the impact of varying engine load was not been considered and studied. In contrast, Raju et al. [29] employed CNT as a nano additive at varying engine load and demonstrated reduced fuel consumption, CO, HC and NO_x emissions. Nevertheless, varying engine speed and particulate matter emissions were not considered in their study.

In summary, it has been previously demonstrated the potential outstanding characteristics of CeO_2 nanopowder as the diesel additive, which can improve the overall engine output and reduce the emissions. However, no research has investigated the influence of the size of CeO_2 nanopowder on the engine performance under various engine operating conditions, which is important for the understanding of the mechanism of how CeO_2 nanopowder reacts with each pollutants during combustion. On the other hand, CNT is also an extraordinary nanomaterial that has the potential to be used as the fuel additive, but studies using it as a single component fuel additive are still limited. Therefore, to make up the current research gaps, the impacts of different sizes of CeO_2 nanopowder on the engine in-cylinder pressure and pollutant emissions are investigated for the first time. Meanwhile, CNT is also studied as a single component fuel additive on the engine performance under various speed and load conditions in this study.

2. Experimental approach

Fuel formulation

The additives used in the study are the multi-wall carbon nanotube with 40 ~ 60 nm diameter size and 2μm length (CNT), Cerium Oxide (CeO_2) nanopowder with the maximum size of 25nm (Ce25) and 50nm (Ce50). The parameters of the three types of nano-additives are listed in Table 1. The CNT is manufactured by the Shenzhen Nanotech Port LTD, and the Ce25 and Ce50 are purchased from the Sigma-Aldrich.com.

Table 1. Key parameters of the nano-additives*

Type	Bulk density (g/cm^3)	Size (nm)	Specific surface area (m^2/g)
CNT	0.22	40 ~ 60 (diameter) 2000 (length)	Min 110
Ce25	0.53	Max 25	30 ~ 50
Ce50	0.53	Max 50	30 ~ 50

*Data provided by the manufactures

The CNT, Ce25 and Ce50 are blended with standard diesel fuel with 40 ppm concentration and then vibrated by an ultrasonic device for two hours to obtain stable and homogeneous mixtures (suspension). Using the processes, the mixtures can keep stable with no deposition for at least one week. After 24 hours' standing, the mixtures are pumped in the fuel tank in the engine test rig as the test fuels. The standard diesel fuel, provided by the Coryton Advanced Fuels Ltd, is used as a reference. The main properties of the tested fuels are listed in Table 2.

Table 2. Properties of the test fuels*

Fuel	Density (kg/m^3) at 15 °C	Viscosity (mPa·s) at 40 °C	Thermal diffusivity (mm^2/s) at 40 °C	LHV (kJ/kg)
DF	840.4	2.82	0.0879	42853
DF-Ce50	840.4	2.82	0.0897	42853
DF-Ce25	840.4	2.81	0.0940	42853
DF-CNT	840.4	2.77	0.1020	42853

*The density and LHV of DF are provided by Coryton, and the viscosity and thermal diffusivity of all test fuels are measured by an NDJ-9S and an LFA 467 Hyper Flash, respectively.

Experimental system

The layout of the engine test rig is illustrated in Fig. **1**.

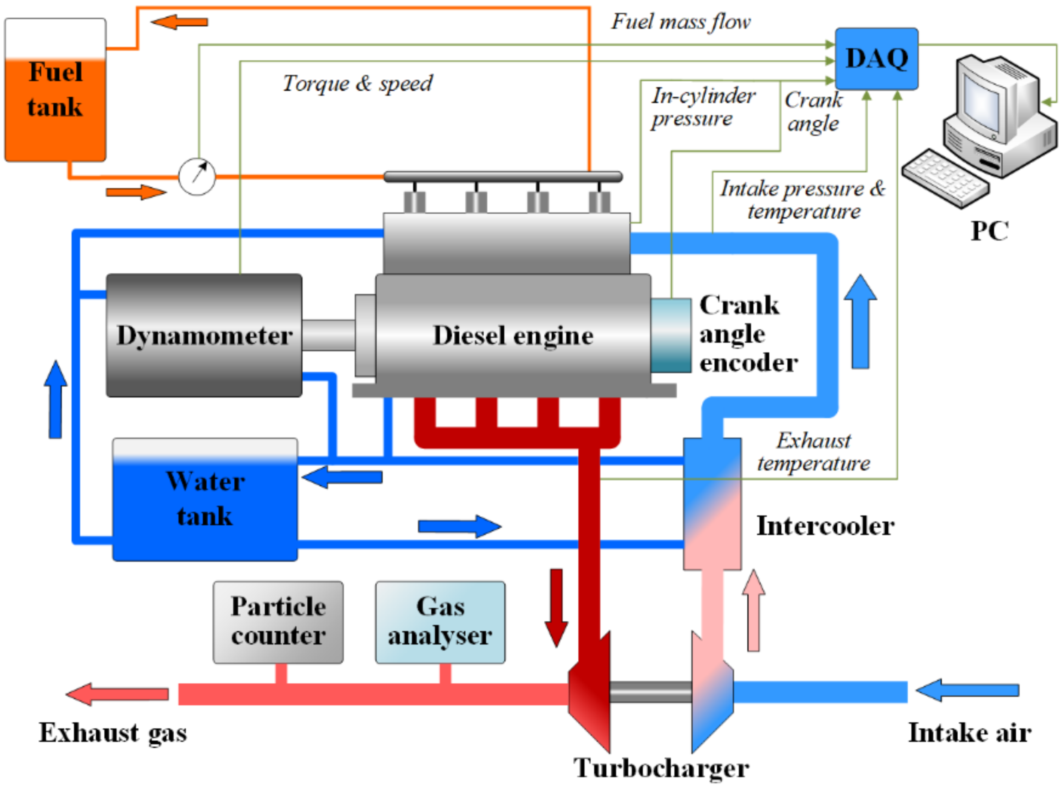


Fig. 1. The engine test rig

The engine is a Cummins ISB4.5 heavy-duty four-stroke diesel engine, where the fuel is compressed by a common rail and injected by four solenoid eight-hole injectors. The real-time mass flow rate of the fuel is measured by a Promass Coriolis flow meter. The engine is connected with a DSG 230kW eddy current dynamometer to control the speed and torque. An AVL 365C crank angle encoder is assembled at the crankshaft to record the crank angle 720 times every cycle, and the in-cylinder pressure is monitored via an AVL high-speed pressure transducer QC34C in the third cylinder. A Horiba MEXA 1600D gas analyser and a Horiba SPCS 1000 particle counter are employed to measure the carbon monoxide (CO), nitrogen oxides (NO_x), unburnt hydrocarbons (HC) and particle number (PN) respectively. The water cooling system is used to cool down the engine, dynamometer, oil, and intake air. All the important parameters, such as torque, speed, crank angle, in-cylinder pressure, intake air pressure and temperature, etc., are collected via a National Instrument data acquisition card PCI-6251 and sent to a PC running a DSG DaTAQ Pro system, which also send commands to the dynamometer and the engine automatically or manually. The range and accuracy of each instrument are listed in Table 4.

Table 3. Specifications of experimental diesel engine

Parameter	Value
Engine model	ISB4.5
Displacement (L)	4.5
Number of cylinders	4
Stroke length (mm)	124
Bore size (mm)	107
Compression ratio	17.3
Injection method	Common rail direct injection
Injection pressure (bar)	1800 bar
Injector type	Solenoid eight-hole injector
Aspiration	Wastegate turbocharger
Speed (rpm)	800 ~ 2500
Torque (Nm)	Max 760 at 1400 ~ 1800 rpm
Power (kW)	Max 152 at 2300 rpm
Emission standard	Euro V

Table 4. Measuring range and accuracy of instruments

Instrument	Measuring range	Accuracy

DSG dynamometer	0 ~ 750 Nm	± 1 Nm & ±10 rpm
AVL 365C crank angle encoder	0 ~ 20000 rpm	±0.5°
AVL QC34C pressure transducer	0 ~ 250 bar	±0.2 bar
Horiba MEXA 1600D gas analyser	3000 ppm (CO) 5000 ppm (NO_x) 1000 ppm (HC)	±1%
Horiba SPCS 1000 CPC	23 ~ 10000nm	±10%
Thermocouples	0 ~ 1200 °C	±0.75%
Promass 80 flow meter	0 ~ 2000 kg/h	±0.15%

Experimental procedure

The European Stationary Cycle (ESC) is employed to run the engine, as shown in Fig. **2**. The idle is 800 rpm and A, B and C are 1490 rpm, 1855 rpm and 2220 rpm respectively. Once a test fuel is pumped in the fuel tank, the engine runs for 20 minutes at 1600 rpm and 25% load to use up all the fuel left in the system in last experiment and warm up the engine, and then goes through all the 13 experimental conditions. After finishing the experiment of the test fuel, the remaining fuel in the system is drained and the lubricant oil is renewed. In the next day, another test fuel is pumped in the fuel tank and the above steps are repeated. Each experimental condition runs for two minutes to record the in-cylinder pressure, fuel flow rate, gaseous emissions and PN emissions. The idling state of 30 seconds is between any two conditions to cool down of the system.

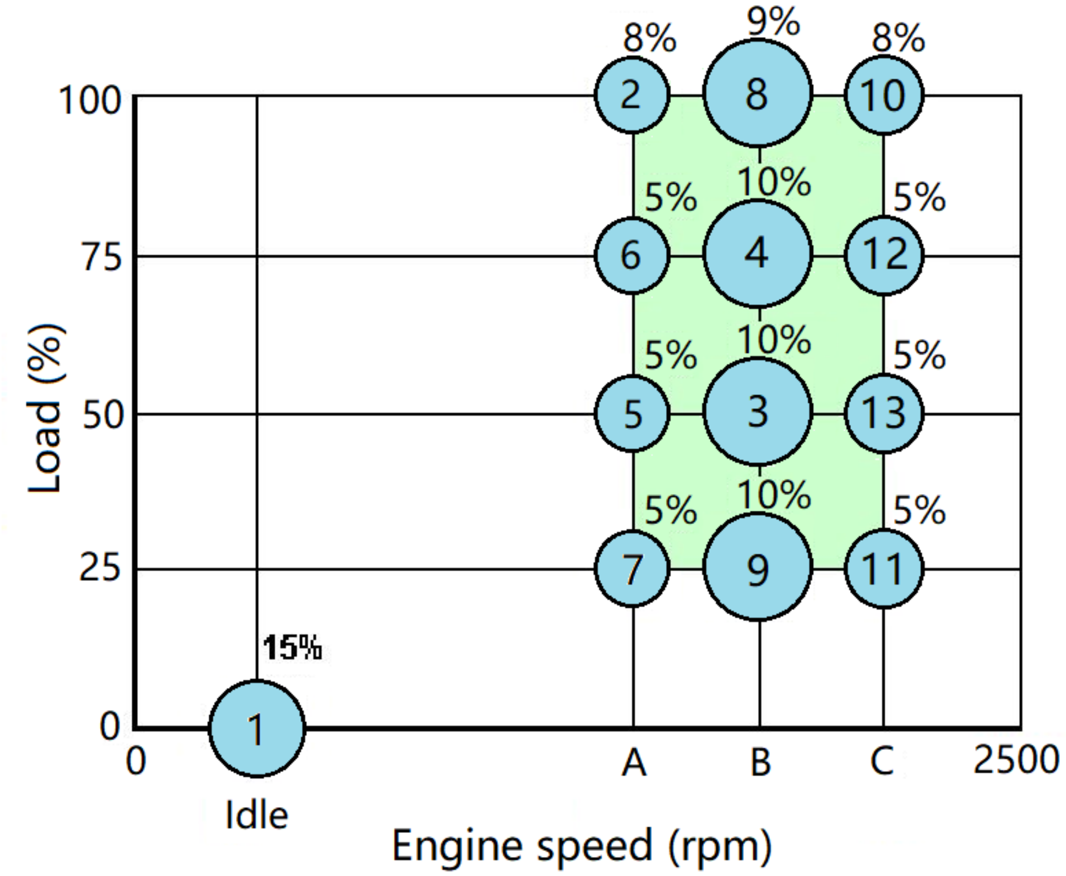


Fig. 2. Experimental conditions according to the ESC

Table 5. Boundary conditions of engine experiments

Fuel temperature (°C)	Air intake temperature (°C)	Cell pressure (bar)	Cell temperature (°C)	Lubricant oil temperature (°C)
40±1	25±0.5	144 ~ 152	40 ~ 43	112 ~ 115

Data processing

The brake specific fuel consumption (BSFC) is the ratio of fuel mass flow rate over the engine brake power. In this paper, the average BSFC (kg/kWh) is employed (Equation (1)), as it indicates the overall level of fuel consumption during the whole experiments.

$$\overline{BSFC} = \frac{\sum m_f \cdot WF_i)}{\sum(Power_i \cdot WF_i)} \qquad (1)$$

The emissions of the gas and PN are measured by concentration with the unit of ppm and #/cm^3 respectively. The specific emission is employed with the unit of g/kWh and #/kWh respectively to compare emissions of various fuels via the following equations.

$$CO_S = \frac{0.000966 \cdot c_{CO} \cdot m_g}{Power} \tag{2}$$

$$NO_{x_S} = \frac{0.001587 \cdot c_{NO_x} \cdot m_g}{Power} \tag{3}$$

$$HC_S = \frac{0.000479 \cdot c_{HC} \cdot m_g}{Power} \tag{4}$$

$$PN_S = \frac{c_{PN} \cdot m_g \cdot 10^6}{Power \cdot \rho_g} \tag{5}$$

Where the c is the concentration of each emission (ppm for gas and #/cm^3 for PN), *Power* is the output power rate of the engine, m_g is the mass flow rate of exhaust gas (kg/h), and ρ_g is the density of exhaust gas which is always considered as 1.293 kg/m^3. The average specific emissions are then obtained by the equations below to indicate the overall level of emissions regardless of engine conditions.

$$\overline{CO} = \frac{0.000966 \cdot \sum(c_{CO,i} \cdot m_{g,i} \cdot WF_i)}{\sum(Power_i \cdot WF_i)} \tag{6}$$

$$\overline{NO_x} = \frac{0.001587 \cdot \sum(c_{NO_x,i} \cdot m_{g,i} \cdot WF_i)}{\sum(Power_i \cdot WF_i)} \tag{7}$$

$$\overline{HC} = \frac{0.000479 \cdot \sum(c_{HC,i} \cdot m_{g,i} \cdot WF_i)}{\sum(Power_i \cdot WF_i)} \tag{8}$$

$$\overline{PN} = \frac{10^6 \cdot \sum(c_{PN,i} \cdot m_{g,i} \cdot WF_i)}{\rho_g \cdot \sum(Power_i \cdot WF_i)} \tag{9}$$

Where the footnote *i* is the order of each condition and WF is the corresponding weight factor (percentage) as shown in Fig. **2**.

3. Results and discussion

In-cylinder behaviour study

In-cylinder pressure is a critical parameter which significantly influences the engine power output, engine noise and NO_x emissions. Fig. **3** to Fig. **8** indicate that the in-cylinder pressure and corresponding HRR of all test fuels increase with the growth of load regardless of the engine speed, which is caused by the more burnt fuel and more radical combustion. Moreover, the combustion duration of all test fuels increases with growing engine load but reduces with increasing engine speed, which is caused by different amount of injected fuel and length of residence time at various loads and speeds. Nevertheless, the existence of nano-additives has no comparable influence on the combustion duration, as they are at quite low concentrations. CeO_2 nanopowder has no significant impact on ignition delay, whilst CNT can enlarge the ignition delay at most conditions, which is determined by its slower evaportion process, as illustrated in Fig. 9.

The differences of in-cylinder pressure and HRR between DF and DF with CeO_2 nanopowder vary under different speeds. At 1490 rpm, the in-cylinder pressure of DF-Ce25 and DF-Ce50 are always higher than that of DF, especially at the engine peak condition. And lower heat release rate (HRR) is also observed for DF at most peaks as shown in Fig. **4**. The reasons are twofold: on one hand, the addition of CeO_2 reduces viscosity and increases thermal diffusivity of DF, which improves spray and then brings in more complete combustion; on the other hand, CeO_2 acts as a catalyst which provides more oxygen to accelerate the combustion reaction via the conversion shown below [30].

$$4CeO_2 \rightleftharpoons 2Ce_2O_3 + O_2 \qquad (9)$$

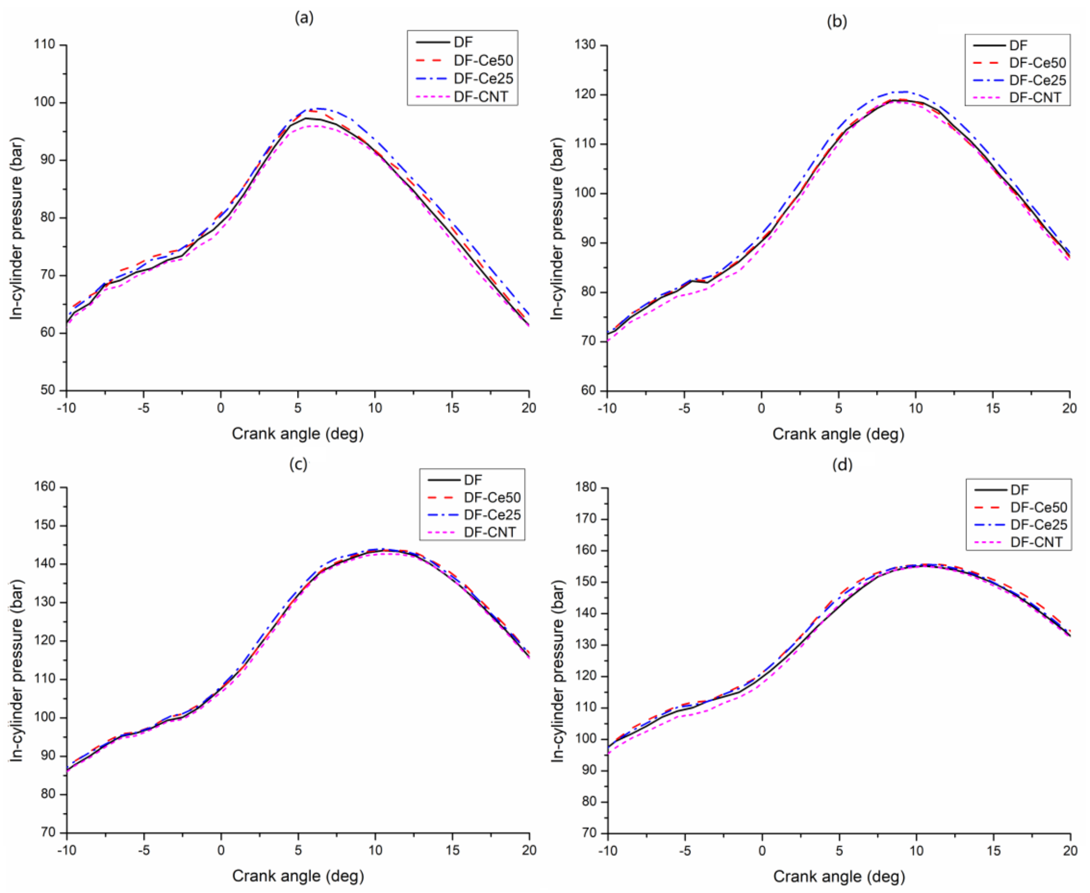


Fig. 3. In-cylinder pressure under 25% (a), 50% (b), 75% (c) and 100% (d) load at 1490 rpm

Fig. **3** also illustrates that the difference between fuels with and without CeO_2 nanopowder additive becomes smaller with increasing load and finally negligible at 100% load. In addition, DF-Ce25 always has higher in-cylinder pressure than DF-Ce50 at the most conditions, because the CeO_2 in the DF-Ce25 has smaller size and larger surface area and thus invokes a higher reaction rate.

When the speed rises to 1855 rpm, the in-cylinder pressure of DF-Ce25 and DF-Ce50 is still higher than that of DF during the main combustion period at most loads, but the difference between them becomes smaller. It is because higher speed shorten the duration of each cycle, and thus the residence time of fuel is not enough for all the catalyst to participate in the reactions. At 2220 rpm engine speed, DF-Ce25 and DF-Ce50 have lower in-cylinder pressure than DF at most loads, because the residence time of fuel is further shortened and many nanoparticles of the CeO_2 act as a nucleus for the unburnt fuel and thus causes incomplete combustion. As CeO_2 nanopowder of 25 nm is smaller and contributes more to the formation of smaller particles, DF-Ce25 sometimes produce lower in-cylinder pressure than DF-Ce50 at high-speed conditions.

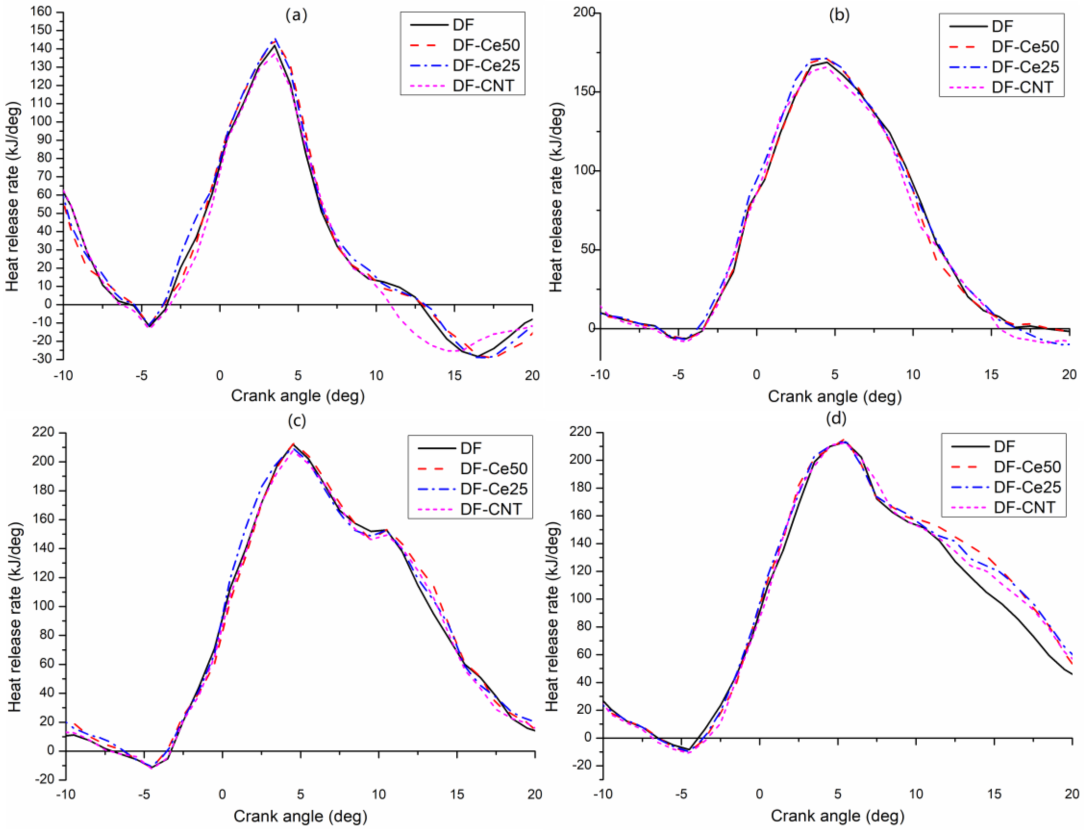


Fig. 4. HRR of test fuels at 1490 rpm and 25% (a), 50% (b), 75% (c) and 100% (d) load

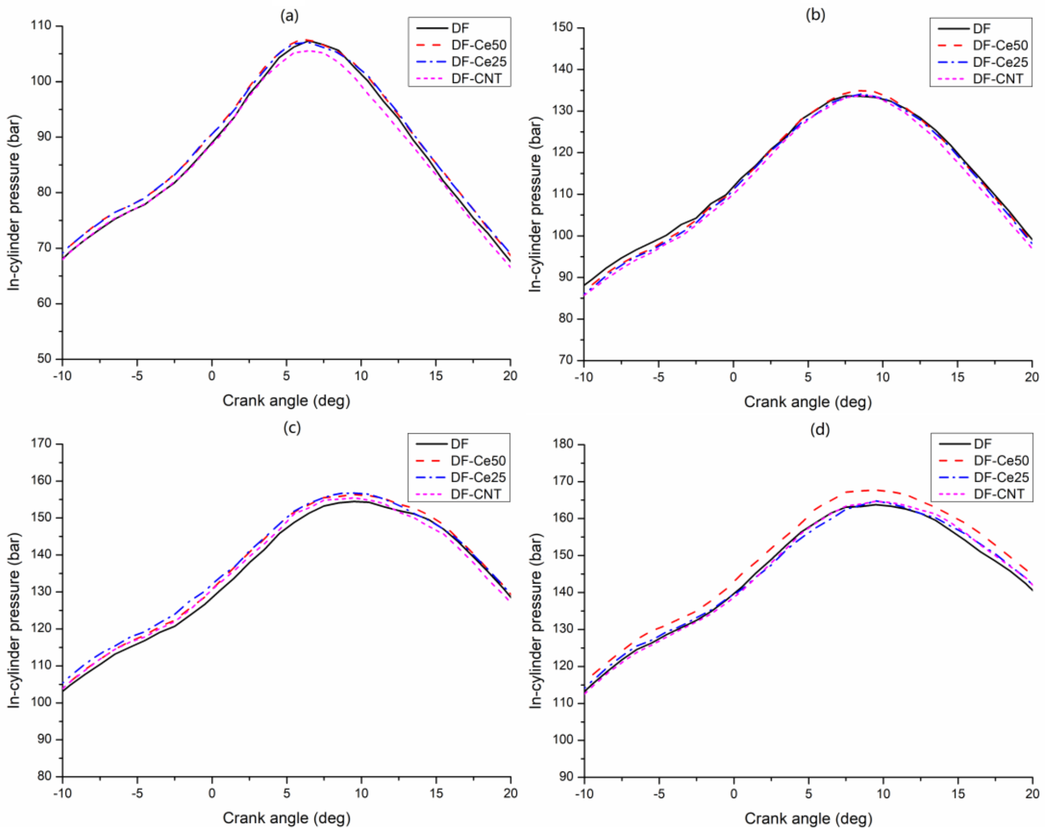


Fig. 5. In-cylinder pressure of test fuels at 1855 rpm and 25% (a), 50% (b), 75% (c) and 100% (d) load

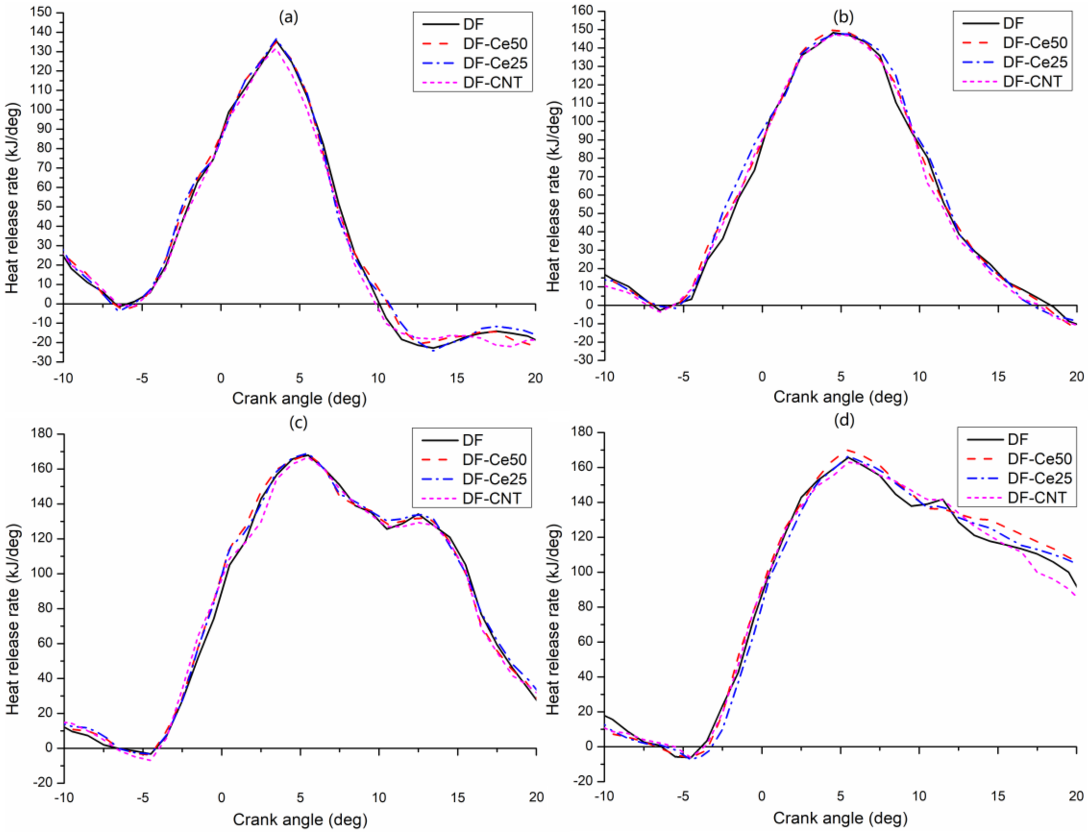


Fig. 6. HRR of test fuels at 1855 rpm and 25% (a), 50% (b), 75% (c) and 100% (d) load

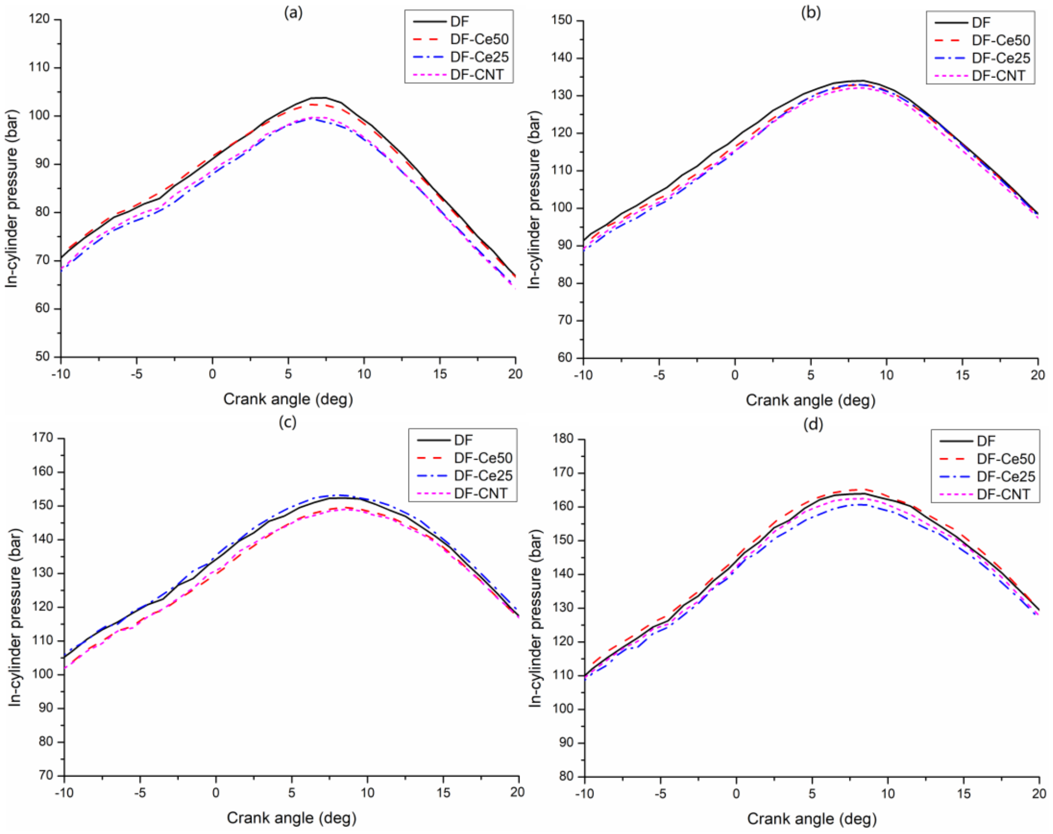


Fig. 7. In-cylinder pressure of test fuels at 2220 rpm and 25% (a), 50% (b), 75% (c) and 100% (d) load

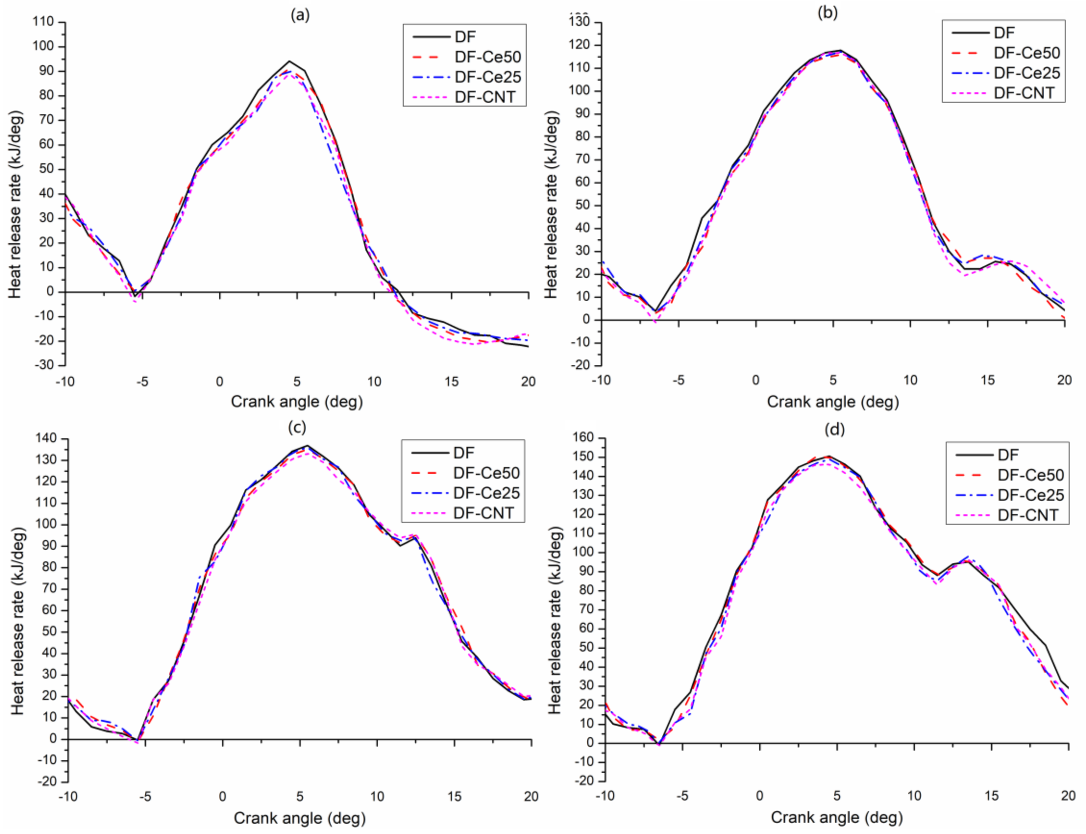


Fig. 8. HRR of test fuels at 2220 rpm and 25% (a), 50% (b), 75% (c) and 100% (d) load

In contrast, DF-CNT produces slightly lower in-cylinder pressure than DF during the main combustion period, especially at the beginning of the combustion (about -5° crank angle) under most load and speed conditions, which also indicates a longer ignition delay. It is likely caused by the unique heat absorption and evaporation process due to the hollow structure of the CNT. After injection, the liquid fuel outside the CNT firstly absorbs heat from the hot air and evaporates, and then the liquid fuel inside the CNT absorbs heat from the heated CNT wall and evaporates, as shown in Fig. **9**. Due to the thick multi-wall structure, the temperature of the CNT wall increases slower than the fuel outside. As a result, the overall duration of the evaporation process is enlarged, which results in longer ignition delay and lower in-cylinder pressure and HRR.

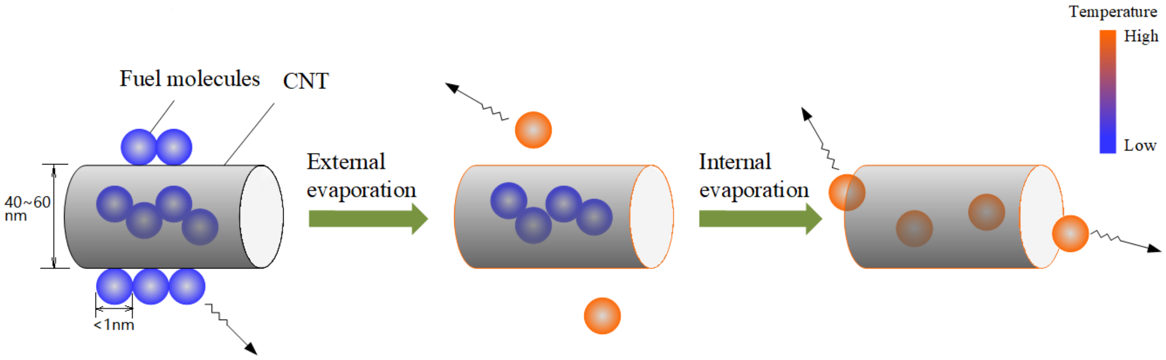


Fig. 9. Illustration of the two-step evaporation of the DF-CNT

Fuel Consumption

As shown in Fig. 10, the average BSFC of all test fuels are closed. It means the additions of nano additives has no comparable influence on fuel consumption of the diesel engine, because the nano additives can only change physical-chemical properties associated with spray and reaction rate of fuel compositions and products. However, the lower heating value

(LHV), which determines power output, cannot be changed by such small amount of additives and thus brings neglectable difference to fuel consumption at the same operating conditions.

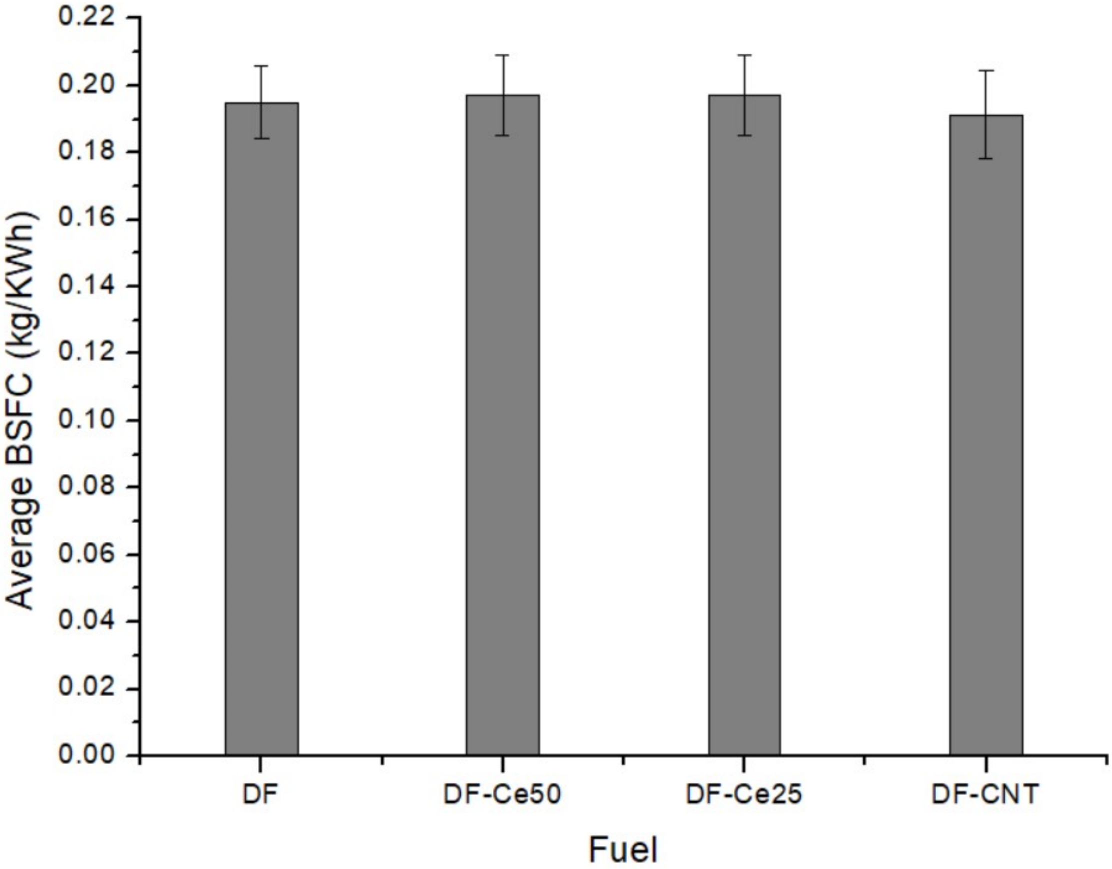


Fig. 10. Average BSFC of nano additives modified DF

CO emissions analysis

CO emissions of all test fuels are illustrated from Fig. 11 (a), (b) and (c), corresponding to the different engine speeds. At 1490 rpm, the CO concentration of all test fuels (dash curves) increases with the increase of engine load at all engine speeds, because the air-fuel ratio becomes lower at high load and thus causes incomplete combustion due to the lack of oxygen. When the engine speed increases to 1855 rpm and 2220 rpm, CO concentration of all test fuels experiences a dramatic drop first and then a growth respect to load. It is because at high speed, the duration of combustion is shorter and thus results in more incomplete combustion, which promotes the formation of the CO. However, the overall reduction of combustion duration reduces the amount of all the products including the CO. Consequently, the CO concentration is impacted by the two controversy effects of engine speed and load.

The specific emission of CO is calculated to compare each tested fuel by the solid curves in Fig. 11. DF-CNT shows advantages in reducing CO emission at almost all speed and load conditions because its modified physical properties such as lower viscosity and higher thermal diffusivity contribute to more uniform fuel-air mixture and more sufficient combustion.

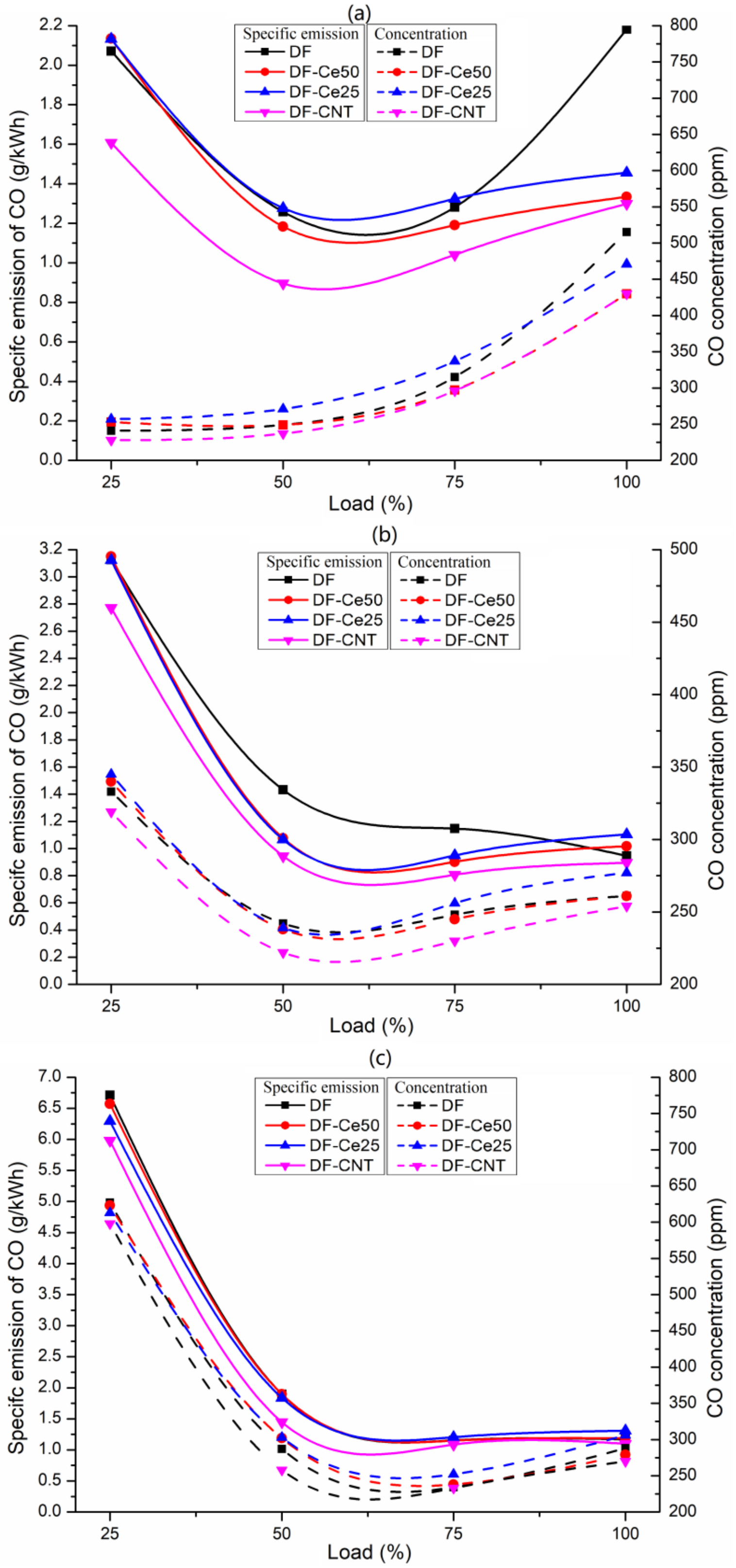


Fig. 11. CO emissions of test fuels at 1490 rpm (a), 1855 rpm (b) and 2220 rpm (c) engine speed

In contrast, the impact of CeO_2 nanopowder on the specific emission of CO is varying with engine condition. At 1490 rpm, the specific CO emission of DF-Ce25 and DF-Ce50 is higher than DF at low load, and then that of DF-Ce50 reduces to lower than DF at about 35% load, whilst that of DF-Ce25 stays higher than DF until about 80% load. When the engine speed grows to 1855 rpm, both DF-Ce50 and DF-Ce25 produce slightly larger or similar amount of specific emission of CO than DF at 25% load, after which their CO emission stays lower than that of DF. The CO emission of DF-Ce25 eventually exceeds that of DF at about 90% load, whilst that of DF-Ce50 surpasses DF at about 95% load. At 2220 rpm, the CO emission of DF-Ce50 and DF-Ce25 can stay lower than that of DF when the load is less than 50%.

According to the literature [31, 32], the impact of CeO_2 on reducing CO emission of standard diesel or biodiesel has a maximum load limit, after which CO emission will be higher than that of DF. Results in this study demonstrate there is also a minimum load limit using CeO_2 as the DF additive, before which the specific emission of CO is also higher than that of the fuel without it. Moreover, both the minimum limit and the maximum limit varies with engine speed and load. Accordingly, the two limits can be defined as the MIN engine limit and the MAX engine limit to the specific emission of CO and illustrate them in Fig. 12. Diesel fuel with the CeO_2 produces lower CO emissions than that without CeO_2 at engine conditions between the two limits. It is obvious that the DF-Ce50 has larger space between the two limits, which means DF-Ce50 is better for the reduction of CO emissions than that of DF-Ce25.

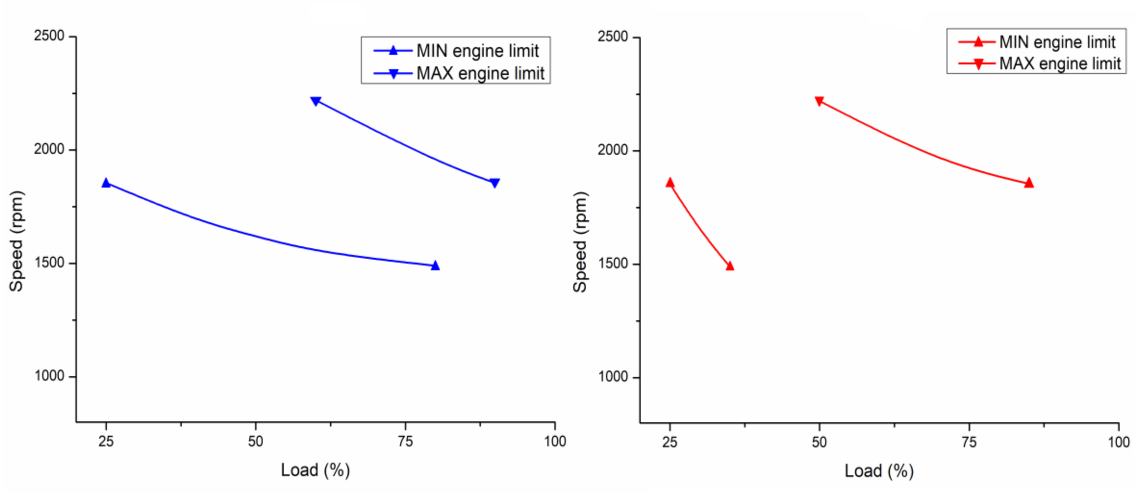


Fig. 12. MIN engine limit and MAX engine limit to the specific emission of CO of the DF-Ce25 (a) and DF-Ce50 (b)

NO_x emissions analysis

At each speed, the NO_x concentration of all test fuels (dash curves) rises with the increase of load, because temperature dominates the formation of NO_x via the thermal path. Therefore, more NO_x is emitted at higher load condition due to the higher in-cylinder temperature as shown by the dash curves plotted in Fig. 13.

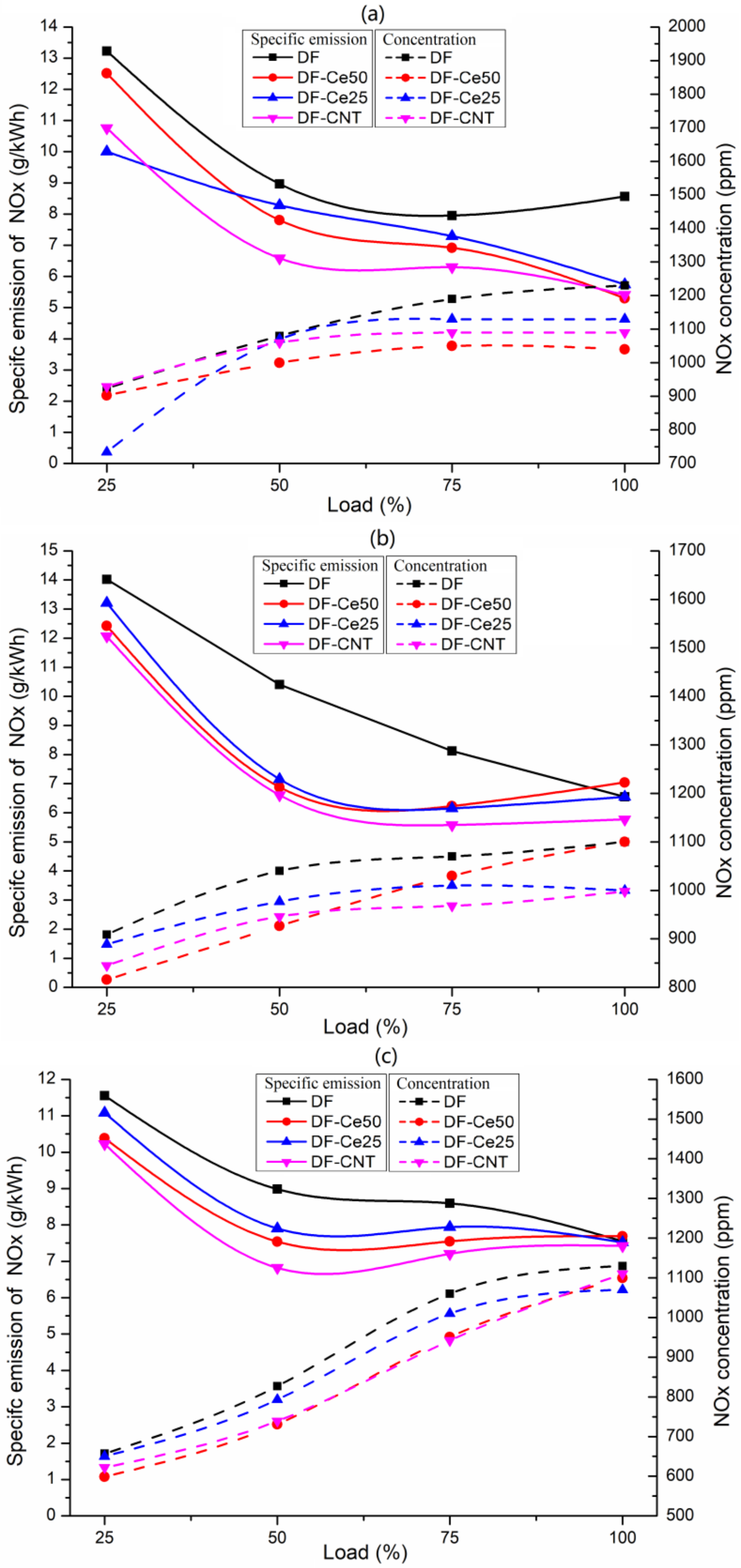


Fig. 13. NO_x emissions of test fuels at 1490 rpm (a), 1855 rpm (b) and 2220 rpm (c) engine speed

Among the tested fuels, the DF-CNT has overall the lowest specific emission of NO_x (solid curves), which can be attributed to the following three reasons. First, DF-CNT produces lower combustion temperature caused by longer fuel evaporation in aforementioned context. Second, DF-CNT generates more uniform spray field due to its lower viscosity and thermal diffusivity. Third, CNT is, in fact, a form of elemental carbon, which can probably act as a deoxidizer during combustion via the equation below and thus prohibit the formation of NO_x.

$$C + 2NO \rightarrow N_2 + CO_2 \tag{10}$$

The fuels with CeO_2 nanopowder also reduce NO_x emissions at the most conditions, because CeO_2 is a catalyst which can convert between CeO_2 (Ce^{+4}) and Ce_2O_3 (Ce^{+3}). During combustion, the CeO_2 help oxidize unburnt fuel compositions, whilst the Ce_2O_3 is used to deoxidize products of strong oxidizing. Consequently, NO_x emissions are mainly reduced via the following equation for DF-Ce25 and DF-Ce50.

$$Ce_2O_3 + 2NO \rightarrow 2CeO_2 + 1/2\,N_2 \tag{11}$$

Moreover, the combustion of DF-Ce25 appears to have a higher specific emission of NO_x (solid curves) than that of DF-Ce50 at the most conditions, which is caused by the different size of CeO_2 nanopowder. Given that CeO_2 converts between CeO_2 and Ce_2O_3 via reversible reactions, a faster rate of the reaction from CeO_2 to Ce_2O_3 will hinder the reaction from Ce_2O_3 to CeO_2. As NO_x is deoxidised by Ce_2O_3, CeO_2 nanopowder of 25 nm experiences higher reaction rate from CeO_2 to Ce_2O_3 due to its larger surface area and in return lowers down the rate for Ce_2O_3 reacting with NO_x.

Results from Fig. 13 also illustrate that all fuels with nano additives have lower specific emissions of NO_x than standard diesel, and the difference between them varies with speed and load. According to the literature [21], the oxygen concentration, residence time and temperature determine the amount of NO_x emissions from the diesel engine. More oxygen and residence time provide more opportunities for N_2 to be oxidised, and higher temperature contributes to the formation of NO_x via the thermal path. Meanwhile, catalysts such as CeO_2 are demonstrated to have better activity at higher temperature [24]. Therefore, the phenomenon of NO_x emissions of all the test fuels should be attributed to the comprehensive effects of the two reasons as previously stated.

At 1490 rpm, the difference of specific emission of NO_x (solid curves) between standard diesel and diesel with nano additives is small at 25% load and then increases to the largest at 100% load. It is because the residence time and amount of air are enough for both the oxidisation of N_2 and the deoxidisation of NO_x at this speed, so temperature is the only factor influencing NO_x emissions of each fuel. When the speed increases to 1855 rpm, the difference at 25% load is small and increases to the largest between 50% and 75% load, and then becomes tiny at 100%. It is probably because the catalysis of CeO_2 nanopowder is not strong at 25% load due to relatively lower combustion temperature, and is improved to its maximum at mid load, after which the catalysis stays at the same level but the formation of NO_x is enhanced. The phenomenon at 2220 rpm is similar to that at 1855 rpm but the overall difference becomes smaller due to short residence time.

HC emissions analysis

HC is the mixture of unburnt fuel compositions and the light products of the thermal degradation of large fuel molecules. It is usually promoted by poor atomization, inadequate combustion and reduced by uniform combustion, oxidants and high temperature. Fig. 14 demonstrates that the HC concentration of all test fuels (dash curves) decreases with increasing load at all speeds. It is because HC is easy to be oxidised by oxidants and to form particulate matters (soot) via dehydrogenation and carbonization at high temperature. It also indicates that the specific emission of HC (solid curves) is increasing when the engine speed rises, which is mainly caused by the inadequate combustion due to shorter residence time.

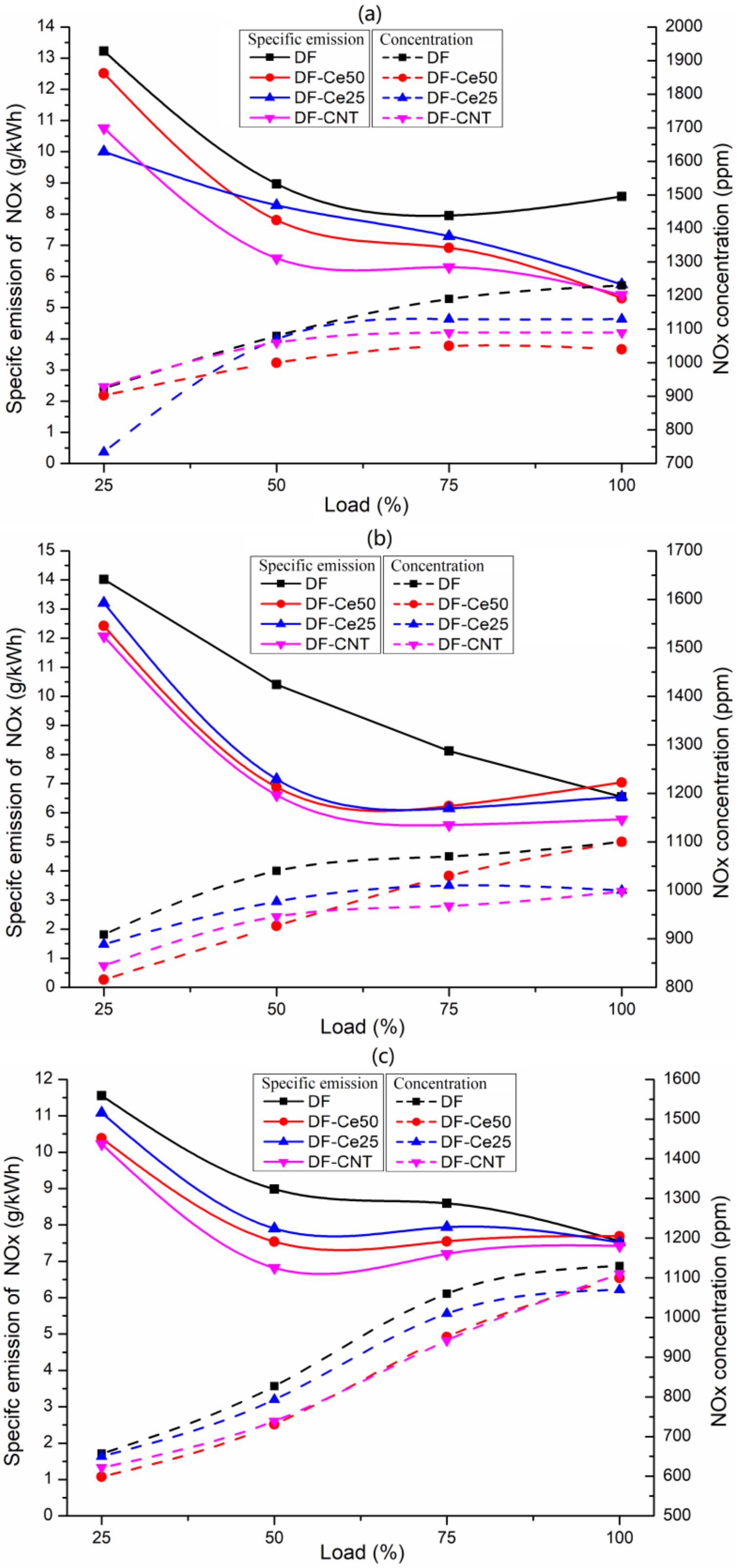


Fig. 14. HC emissions of test fuels at 1490 rpm (a), 1855 rpm (b) and 2220 rpm (c) engine speed

As shown in Fig. 14, fuels with nano additives have a lower specific emission of HC (solid curves) than standard diesel fuel. However, the difference between them is large at 1490 rpm and 1855 rpm engine speed but reduces at 2220 rpm, which is because the shorter residence time limits the reaction of additives. Among the fuels with Nano additives, DF-CNT has the lowest specific emission of HC in most conditions. As described in aforementioned paragraphs, DF-CNT generates more uniform spray field due to its lower viscosity and thermal diffusivity and thus experiences relatively more homogeneous combustion than others. As a result, despite lower in-cylinder pressure, few fuel-rich zones exist during DF-CNT combustion and thus less unburnt fuel is emitted. DF-Ce50 and DF-Ce25 produce lower HC emissions than DF mainly due to the catalytic reaction of CeO_2 as shown in the equation below.

$$(2x+y)CeO_2 + C_xH_y \rightarrow \left[\frac{2x+y}{2}\right] Ce_2O_3 + \frac{x}{2}CO_2 + \frac{y}{2}H_2O \tag{12}$$

Where CeO_2 act as the oxidant for HC, and the products Ce_2O_3 participate in the deoxidization of NO_x. DF-Ce25 produces slightly lower HC due to its smaller size and larger specific surface area of nanopowder, which provide more opportunities for CeO_2 to react with HC.

PN emissions

Particulate matters (PM) are usually formed by the dehydrogenation and carbonization of unburnt fuels at high temperature and low oxygen conditions. Therefore, high load and the existence of nuclei will promote the formation of PM, whilst more oxygen content and longer residence time will consume the amount of PM. In this study, the particulate number (PN) of each test fuel at various conditions are shown in Fig. 15. It illustrates that the PN concentration of all test fuels (dash curves) increases with the rise of the load at each engine speed. Because high load enables fuel compositions more likely to experience incomplete combustion and thus form more PMs due to the relatively fuel-rich condition. Furthermore, high load also promotes the formation of smaller PMs, as the larger ones are easy to be burnt at a high temperature. Meanwhile, as the shorter residence time reduces the chance of complete combustion of PMs, the overall level of PN concentration grows as the engine speed increase from 1490 rpm to 2220 rpm.

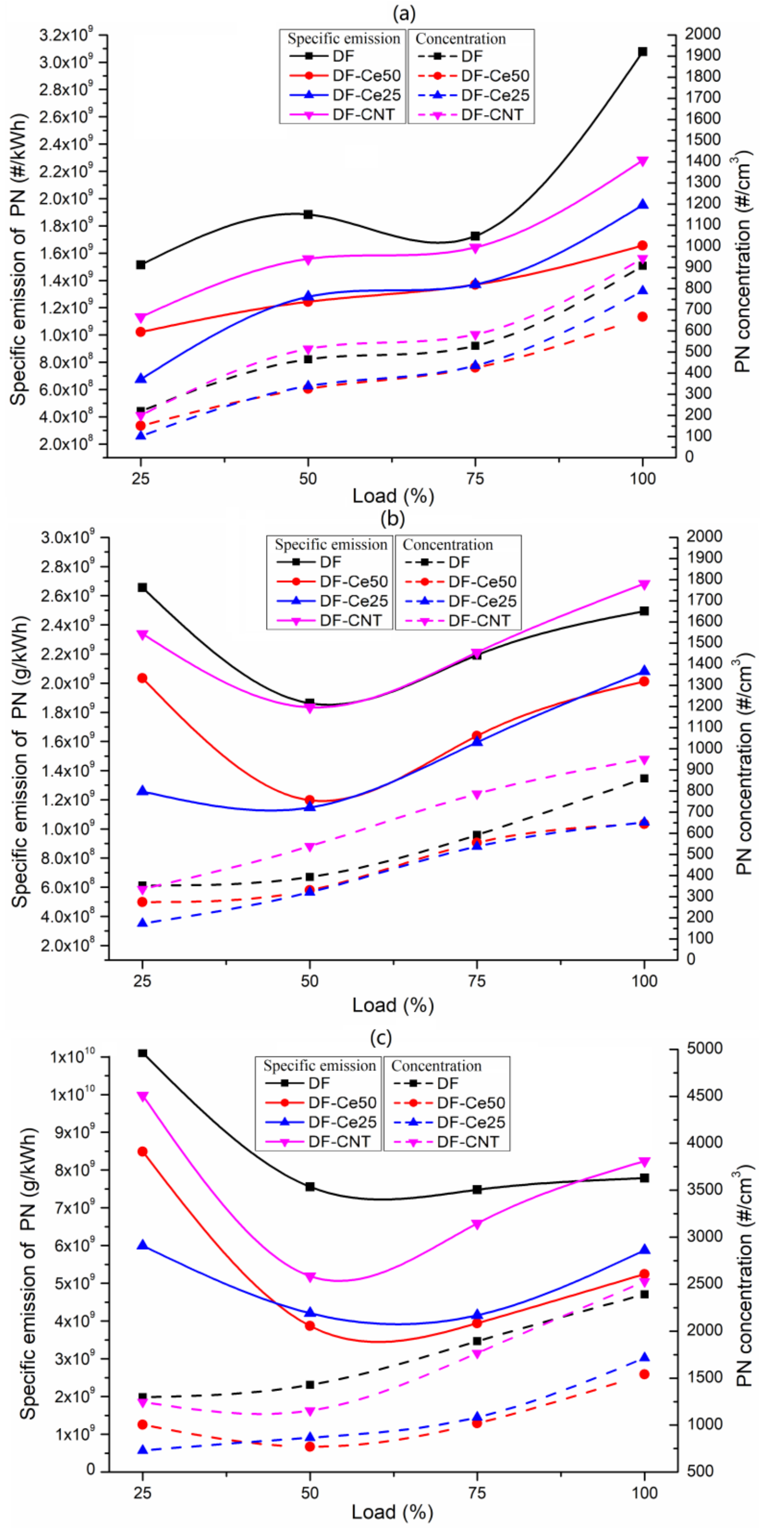


Fig. 15. PN emissions of test fuels at 1490 rpm (a), 1855 rpm (b) and 2220 rpm (c) engine speed

DF-CNT has a lower specific emission of PN (solid curves) at all loads when the engine speed is 1490 rpm. However, when the engine speed increases to 1855 rpm and 2220 rpm, the specific emission of PN of DF-CNT exceeds that of DF at high load (between 75% and

100%). On one hand, DF-CNT experiences improved spray and lower combustion temperature as described in the aforementioned context, which is helpful in the reduction of PN emissions. On the other hand, CNT can act as the nucleus for the formation of particulate matters. Accordingly, the PN emissions of CNT is the comprehensive results of the two contradictory effects. At low speed, PMs have more time to be burnt, especially in a more uniform air-fuel mixture and lower temperature brought by DF-CNT, so the specific emission of PN of DF-CNT stays at a lower level than that of DF. At high speed, the residence time is not enough to burn most particulate matters, and thus CNT has the chance to participate in the formation of particulate matters as the nucleus at high load, which enables more PN emissions.

In terms of DF-Ce25 and DF-Ce50, their specific emission of PN (solid curves) are both significantly lower than DF at all conditions, regardless of varying load and speed. The reasons are twofold: First, CeO_2 can oxidize particulate matters via Equation (13), which consumes a large amount of PMs.

$$4CeO_2 + C_{PM} \rightarrow 2Ce_2O_3 + CO_2 \qquad (13)$$

Second, CeO_2 consumes some HCs via Equation (12) before they convert to PMs through dehydrogenation and carbonization. However, the CeO_2 nanoparticle is also a type of nucleus, which can contribute to the formation of PM under some conditions. It can explain the reason that DF-Ce25 has a lower specific emission of PN than DF-Ce50 at relatively low load but it becomes higher at high load because the CeO_2 of smaller size is more easily to aggregate unburnt fuel molecules to form smaller PMs which is usually of larger amount than the bigger PMs.

Average specific emissions analysis

In order to evaluate the overall level of emissions, the average specific emissions of all pollutants are calculated via Equation (5) to (8). As demonstrated in Fig. 16, all fuels with nano-additives have lower average specific emissions of CO, NO_x, HC and PN than standard diesel fuel due to their modified physical-chemical properties.

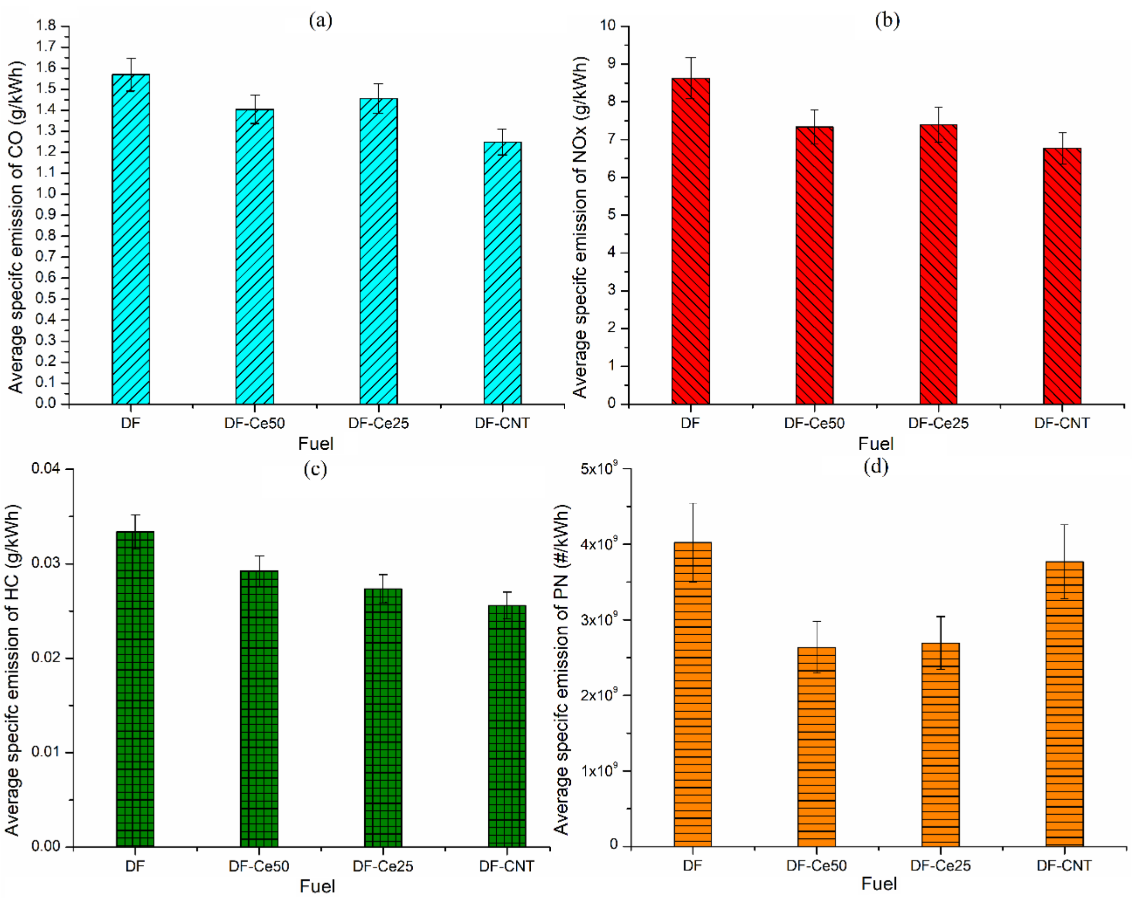
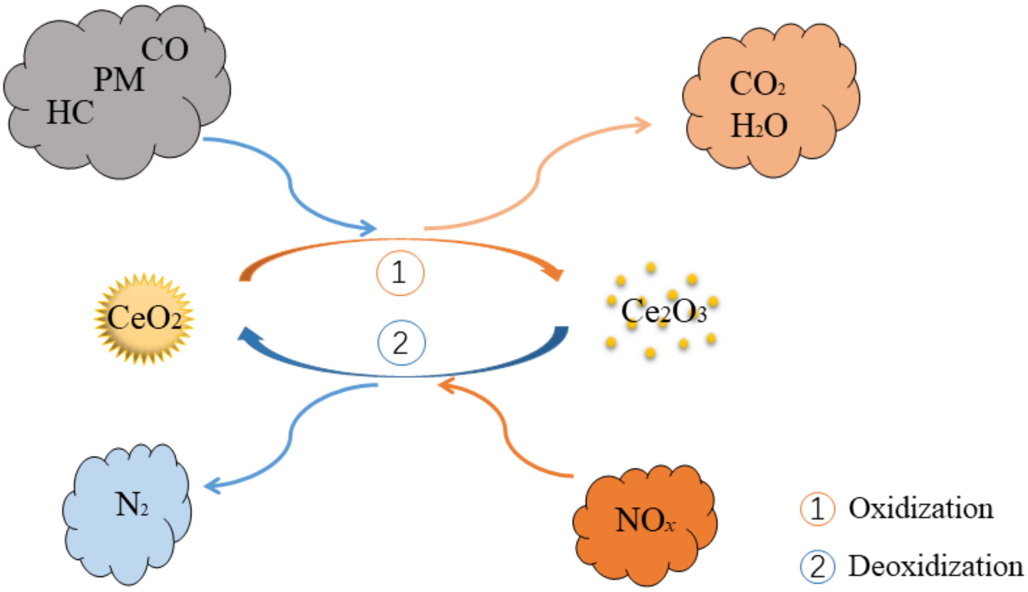


Fig. 16. Average specific emission of CO (a), NO_x (b), HC (c) and PN (d) of test fuels

Among all the fuels with nano-additives, DF-CNT has the lowest average specific emissions of CO, NO_x and HC (20%, 21% and 22.6% lower than DF respectively), because it generates lower combustion temperature caused by its unique two-step evaporation and more uniform combustion due to its lower viscosity and higher thermal diffusivity. However, its average specific emission of PN is the highest among the three modified fuels, which is only 5.5% lower than DF, because CNT is likely to act as the nucleus for the formation of particulate matters at high load and high-speed conditions despite its improved spray quality. Both DF-Ce25 and DF-Ce50 have a lower level of emissions of all pollutants than DF, but DF-Ce25 is slightly higher on CO and NO_x and slightly lower on HC than DF-Ce50. CeO_2 converts to Ce_2O_3 via reversible reactions, so a faster rate of the reaction from CeO_2 to Ce_2O_3 will suppress the reaction from Ce_2O_3 to CeO_2, vice versa. As HC and PM can be oxidized by CeO_2 and NO_x is deoxidized by Ce_2O_3, CeO_2 powder of 25 nm experiences higher reaction rate from CeO_2 to Ce_2O_3 due to its larger surface area and in return lowers down the rate for Ce_2O_3 reacting with NO_x, as illustrated in Fig. 17. Despite the oxidization of PMs by CeO_2, the CeO_2 nanopowder of smaller size is a better type of nucleus forming smaller PM (larger amount), and thus enables DF-Ce25 to emit slightly higher PN than DF-Ce50.



⋆Smaller CeO_2 nanopowder has higher reaction rate of ① and thus hinders reaction ②, vice versa.

Fig. 17. Illustration of the catalytic reaction of CeO_2 nanopowder

4. Conclusions

This research investigated the impacts of using carbon nanotubes (CNT) and CeO_2 nanopowder with two different sizes as diesel fuel additives on the performance of a diesel engine in terms of in-cylinder pressure and pollutant emissions. The key conclusions can be summarised as follows:

1. CNT can slightly lower down the in-cylinder pressure during the main combustion period under most conditions because the evaporation of DF-CNT absorbs more heat during combustion. In contrast, CeO_2 nanopowder improves in-cylinder pressure at low speed due to the improved fuel spray and accelerated combustion reactions.
2. NO_x and PN emissions of all test fuels rise with the increase of engine load due to high temperature. HC emissions drop with increasing load due to oxidisation and the conversion to particulate matters at high temperature, but increase with rising engine

speed caused by the inadequate combustion.

3. CNT reduces the average specific emissions of CO, HC, NO_x and PN by 20%, 22.6%, 21% and 5.5% respectively. The reduced CO and HC are caused by the more uniform fuel-air mixture and more sufficient combustion, whilst the reduced NO_x is attributed to the lower combustion temperature, improved spray and deoxidisation of NO_x. The reduction of PN is the comprehensive results of two contradictory effects: the improved spray and lower combustion temperature, and its nucleation effect.
4. CeO_2 nanopowder decreases the average specific emissions of NO_x, HC and PN, because it can oxidize HC and PM and deoxidize NO_x via reversible reactions, whilst CO can only be reduced in a certain engine condition range.
5. CeO_2 nanopowder of 50 nm size reduces less CO emissions and HC emissions but more NO_x than that of 25 nm size, because smaller CeO_2 nanopowder has a higher reaction rate of CeO_2 oxidizing HC and CO due to its larger surface area and in return reduces the reaction rate of the Ce_2O_3 deoxidizing NO_x.
6. CeO_2 nanopowder of 50 nm size can reduce more average specific emission of PN than that of 25 nm size, because smaller size is more easily to aggregate unburnt fuel molecules to form smaller PMs of a larger amount, although CeO_2 can either oxidize existing particulate matters or consumes some HCs before they convert to PMs.

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References

[1] Mamakos A, Martini G, Manfredi U. Assessment of the legislated particle number measurement procedure for a Euro 5 and a Euro 6 compliant diesel passenger cars under regulated and unregulated conditions. Journal of Aerosol Science. 2013;55:31-47.

[2] COMMISSION REGULATION (EU) 2016/1718. In: (EU) CR, editor.: Commission Regulation (EU); 2016.

[3] Amara AB, Dauphin R, Babiker H, Viollet Y, Chang J, Jeuland N, et al. Revisiting diesel fuel formulation from Petroleum light and middle refinery streams based on optimized engine behavior. Fuel. 2016;174:63-75.

[4] Chen L, Zhang Z, Gong W, Liang Z. Quantifying the effects of fuel compositions on GDI-derived particle emissions using the optimal mixture design of experiments. Fuel. 2015;154:252-60.

[5] Chen L, Zhang Z, Lu Y, Zhang C, Zhang X, Zhang C, et al. Experimental study of the gaseous and particulate matter emissions from a gas turbine combustor burning butyl butyrate and ethanol blends. Applied energy. 2017;195:693-701.

[6] Fayyazbakhsh A, Pirouzfar V. Investigating the influence of additives-fuel on diesel engine performance and emissions: Analytical modeling and experimental validation. Fuel. 2016;171:167-77.

[7] Khorramshokouh S, Pirouzfar V, Kazerouni Y, Fayyazbakhsh A, Abedini R. Improving the Properties and Engine Performance of Diesel–Methanol–Nanoparticle Blend Fuels via Optimization of the Emissions and Engine Performance. Energy & Fuels. 2016;30:8200-8.

[8] Fayyazbakhsh A, Pirouzfar VJR, Reviews SE. Comprehensive overview on diesel additives to reduce emissions, enhance fuel properties and improve engine performance. 2017;74:891-901.

[9] Choi SU, Eastman JA. Enhancing thermal conductivity of fluids with nanoparticles. Argonne National Lab., IL (United States); 1995.

[10] Gumus S, Ozcan H, Ozbey M, Topaloglu B. Aluminum oxide and copper oxide nanodiesel fuel properties and usage in a compression ignition engine. Fuel. 2016;163:80-7.

[11] Saxena V, Kumar N, Saxena VK. A comprehensive review on combustion and stability aspects of metal nanoparticles and its additive effect on diesel and biodiesel fuelled CI engine. Renewable and Sustainable Energy Reviews. 2017;70:563-88.

[12] Soudagar MEM, Nikghazali N, Kalam MA, Badruddin IA, Banapurmath NR, Akram NJEC, et al. The effect of nano-additives in diesel-biodiesel fuel blends: A comprehensive review on stability, engine

performance and emission characteristics. 2018;178:146-77.

[13] Sabourin JL, Yetter RA, Parimi VS. Exploring the effects of nanostructured particles on liquid nitromethane combustion. Journal of Propulsion and Power. 2010;26:1006-15.

[14] Gan Y, Qiao L. Combustion characteristics of fuel droplets with addition of nano and micron-sized aluminum particles. Combustion and Flame. 2011;158:354-68.

[15] Mehta RN, Chakraborty M, Parikh PA. Nanofuels: Combustion, engine performance and emissions. Fuel. 2014;120:91-7.

[16] Balamurugan S, Sajith V. Stabilization Studies of Zirconium-Cerium Oxide Nanoparticle-Diesel Suspension. Advanced Materials Research. 2013;685:128-33.

[17] Nanthagopal K, Ashok B, Tamilarasu A, Johny A, Mohan AJEC, Management. Influence on the effect of zinc oxide and titanium dioxide nanoparticles as an additive with Calophyllum inophyllum methyl ester in a CI engine. 2017;146:8-19.

[18] Valihesari M, Pirouzfar V, Ommi F, Zamankhan F. Investigating the effect of Fe2O3 and TiO2 nanoparticle and engine variables on the gasoline engine performance through statistical analysis. Fuel. 2019;254:115618.

[19] Zamankhan F, Pirouzfar V, Ommi F, Valihesari MJES, Research P. Investigating the effect of MgO and CeO 2 metal nanoparticle on the gasoline fuel properties: empirical modeling and process optimization by surface methodology. 2018;25:22889-902.

[20] Vairamuthu G, Sundarapandian S, Kailasanathan C, Thangagiri B. Experimental investigation on the effects of cerium oxide nanoparticle on calophyllum inophyllum (Punnai) biodiesel blended with diesel fuel in DI diesel engine modified by nozzle geometry. Journal of the Energy Institute. 2016;89:668-82.

[21] Saraee HS, Taghavifar H, Jafarmadar S. Experimental and numerical consideration of the effect of CeO2 nanoparticles on diesel engine performance and exhaust emission with the aid of artificial neural network. Applied Thermal Engineering. 2017;113:663-72.

[22] Aghbashlo M, Tabatabaei M, Khalife E, Najafi B, Mirsalim SM, Gharehghani A, et al. A novel emulsion fuel containing aqueous nano cerium oxide additive in diesel–biodiesel blends to improve diesel engines performance and reduce exhaust emissions: Part II–Exergetic analysis. Fuel. 2017;205:262-71.

[23] Khalife E, Tabatabaei M, Najafi B, Mirsalim SM, Gharehghani A, Mohammadi P, et al. A novel emulsion fuel containing aqueous nano cerium oxide additive in diesel–biodiesel blends to improve diesel engines performance and reduce exhaust emissions: Part I–Experimental analysis. Fuel. 2017;207:741-50.

[24] Gross MS, Sánchez BS, Querini CA. Diesel particulate matter combustion with CeO2 as catalyst. Part II: Kinetic and reaction mechanism. Chemical engineering journal. 2011;168:413-9.

[25] Mirzajanzadeh M, Tabatabaei M, Ardjmand M, Rashidi A, Ghobadian B, Barkhi M, et al. A novel soluble nano-catalysts in diesel–biodiesel fuel blends to improve diesel engines performance and reduce exhaust emissions. Fuel. 2015;139:374-82.

[26] Najafi G. Diesel engine combustion characteristics using nano-particles in biodiesel-diesel blends. Fuel. 2018;212:668-78.

[27] Heydari-Maleney K, Taghizadeh-Alisaraei A, Ghobadian B, Abbaszadeh-Mayvan A. Analyzing and evaluation of carbon nanotubes additives to diesohol-B2 fuels on performance and emission of diesel engines. Fuel. 2017;196:110-23.

[28] Ghanbari M, Najafi G, Ghobadian B, Yusaf T, Carlucci A, Kiani MKD. Performance and emission characteristics of a CI engine using nano particles additives in biodiesel-diesel blends and modeling with GP approach. Fuel. 2017;202:699-716.

[29] Raju VD, Kishore PS, Nanthagopal K, Ashok BJEC, Management. An experimental study on the effect

of nanoparticles with novel tamarind seed methyl ester for diesel engine applications. 2018;164:655-66.

[30] Hajjari M, Ardjmand M, Tabatabaei M. Experimental investigation of the effect of cerium oxide nanoparticles as a combustion-improving additive on biodiesel oxidative stability: mechanism. RSC Advances. 2014;4:14352-6.

[31] Ganesh D, Gowrishankar G. Effect of nano-fuel additive on emission reduction in a biodiesel fuelled CI engine. Electrical and Control Engineering (ICECE), 2011 International Conference on: IEEE; 2011. p. 3453-9.

[32] Manikandan R, Sethuraman N. Experimental investigation of nano additive ceric oxide (CeO2)-ethanol blend on single cylinder four stroke diesel engine. IJRDET. 2014;3:24-8.