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# Study on the combustion and emission characteristics of a compression ignition engine using diesel/ethanol blend with carbon nanoadditives

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Abstract: This article focuses on the effects of adding different types (graphene oxides, multi-layered 4 graphene oxides, multi-walled carbon nanotubes) and dosages (25ppm, 100ppm) of renewable carbon 5 nanoparticles to the diesel/ethanol blend towards the combustion and emission characteristics of a 6 compression-ignition engine. The research showed that a shortened ignition delay was brought about 7 due to the presence of carbon nanoparticles, with the most pronounced effect achieved by multi-walled 8 carbon nanotubes. Regarding in-cylinder combustion, the inclusion of carbon nanoparticles induced 9 an enhancement to the combustion progress, associated with increments in peak cylinder gas pressure 10 and peak heat release rate and a decrement in combustion duration, most notably accomplished by 11 graphene oxides. Moreover, the engine exhibits lower fuel consumption and better fuel utilization 12 based on the carbon nanoparticles addition, where the nano-fuels with graphene oxides possess the 13 minimum brake specific fuel consumption and maximum brake thermal efficiency. Concerning the 14 abatement effect, by applying carbon nanoparticles, emissions of CO, HC and soot were decreased by 15 37.95%, 45.18% and 47.83%, respectively, however, a slight increase in NOx emissions also occurred. 16 In particular, multi-walled carbon nanotubes offered the most significant mitigations in CO and HC, 17 while graphene oxides achieved the greatest abatement in soot emissions. 18

*Keywords*: Diesel engines, Renewable Carbon nanoadditives, Renewable Ethanol, Combustion,
Performance, Emissions

## 1 1. Introduction

In recent years, accompanied by tremendous economic expansion and explosive technological 2 3 evolution, fossil energy scarcity has become a serious worldwide crisis. Against this backdrop, renewable energy sources are gradually becoming an overwhelming substitute for non-renewable 4 5 energy sources. As one of the most widely used energy conversion devices in agricultural machinery and power generation [1, 2], diesel engines are characterized by high thermal efficiency, high reliability 6 and low maintenance costs. At present, a variety of innovative technologies have been employed to 7 enable the efficient and clean combustion of diesel, specifically combustion improvement [3, 4] and 8 9 engine design modification [5]. Among the techniques, combustion improvement is undoubtedly desirable as it has the minimum complication implicated, which could be attained through optimizing 10 fuel properties and improving injection strategies. Therefore, in the broad backdrop to the rapid take-11 12 off of renewable energies, the employment of renewable and clean alternative fuels in diesel engines presents an essential approach. Alcohol-based alternative fuels, widely recognized for their nature to 13 enhance fuel combustion, have been recently advocated for application in commercial vehicles by the 14 15 policies of many countries and agencies [6, 7]. Among these, available from sugar in vegetables through alcoholic fermentation [8], ethanol, as a renewable biomass-based alternative fuel, has gained 16 the interest of many researchers. With a high octane number, ethanol is widely incorporated into 17 gasoline to obtain increased torque for spark-ignition engines without any knock [9, 10]. In terms of 18 diesel engines, however, the lower viscosity and cetane number of ethanol prevents it from igniting 19 without auxiliary ignition, which could be mitigated by blending with diesel fuel. While the cylinder 20 21 co-combustion from diesel fuel and ethanol is available through direct mixing [11] or double-jet design [12, 13], as no engine modification is required, direct mixing is clearly a more affordable way. 22

According to previous experimental studies [14, 15], used as a diesel fuel additive, ethanol was found 1 to accelerate the combustion process and minimize soot emission. However, the fuel evaporation 2 3 difficulty and energy content deprivation create obstacles to further utilization as a diesel alternative. The research conducted by Rakopoulos et al. [8] reported an increased ignition delay due to the low 4 5 cetane number of ethanol. Furthermore, Kumar et al. [16] noticed that the inclusion of ethanol lowered the calorific value of the fuel, which elevated the brake specific fuel consumption (BSFC). Moreover, 6 based on the cooling effect and prolonged ignition delay formed by the low cetane number and calorific 7 value of ethanol, such issues as increased HC and CO emissions were revealed to arise with the 8 9 presence of ethanol [14, 17]. Confronting the problems shared by such alcohol substitution fuels, in the investigation conducted by Chen et al. [18], the adjustment in the fuel injection timing has been 10 adopted. However, their results indicated that the injection timing, once adjusted, was found to cause 11 12 an increase in either NOx emissions or soot emissions, probably not an unquestionably absolute abatement strategy. 13

In recent years, supported by advances in nanotechnology, experimental works around the 14 application of nano-fuel additives have come to the forefront. As many studies reported, the 15 introduction of nanoparticles has been proven to shorten the ignition delay and improve the fuel 16 economy, together with decreasing emissions. The research carried out by Simhadri et al. [19] focused 17 on the impacts of TiO<sub>2</sub> on the engine fueled with diesel fuel containing 20%vol Mahua biodiesel under 18 various injection pressures. The results indicated that TiO<sub>2</sub> nanoparticles effectively improved the 19 ignition quality and the fuel economy, especially at low injection pressure. Besides, their emissions 20 were also significantly reduced, with decrements by 31.5%, 38.5%, 9.1% and 5.5% in CO, HC, smoke 21 opacity and NOx. These could be ascribed to the favorable assets of nanoparticles, including 22

evaporation acceleration [20], combustion enhancement [21] and fuel distribution improvement 1 (strengthened micro-explosion [22]), which is associated with the high specific area and high thermal 2 3 conductivity of nanoparticles. Comprised of metals with high thermal conductivity, metallic nanomaterials have demonstrated desirable enhancements upon engine combustion and emissions in 4 5 previous studies as a fuel additive. Rajesh et al. [23] revealed increments in peak in-cylinder pressure and peak heat release rate by 8.82% and 16.4%, respectively, upon the incorporation of alumina 6 nanoparticles into biodiesel, coupled with reductions in combustion duration and ignition delay. They 7 interpreted the efficacy of the nano-additives in terms of the catalytic behavior of the nanoparticles 8 9 that accelerated the combustion rate. Besides, the addition of metal nanoparticles cut down the emissions in CO, HC and smoke, yet for the most part, they present remarkable compensation above 10 NOx. As an example, in the experiment conducted by Rejish et al. [23], the inclusion of alumina 11 12 particles obtained reductions in the ranges of 25%-33.3% and 19.4%-26.5% in CO and HC, respectively, and NOx was increased in the range of 118.2%-23.5%. In addition, during the 13 employment as fuel additives for metallic nanomaterials, the exhaust gas from the combustion would 14 15 contain the metal residual as the metal particles couldn't burn up in the cylinder, which would pose a hazard to human beings and the environment [24]. Consequently, although the effect of metal 16 nanoparticles as fuel additives is absolutely favorable, the application of the fuels with the addition of 17 metal nanoparticles requires further development and cautious consideration in view of the fact that 18 they can exacerbate the toxicity of vehicle exhaust. Therefore, given the growing scarcity of fossil 19 fuels, in order to promote the wide application of ethanol fuels, an environment-friendly nano-additive 20 21 without introducing new impurities into engine exhaust is expected.

22 Carbon-based nanomaterials, as renewable materials, can be prepared by pyrolysis or salt-based

methods from agricultural/agro-industrial wastes and municipal wastes [25, 26]. Importantly, carbon-1 based nanoparticles are structured by carbon atoms, hence their utilization as fuel additives is less toxic 2 3 than metal nanoparticles. Moreover, compared with metal nanoparticles, carbon nanoparticles are less prone to form aggregation since there is less magnetic attraction between nanoparticles [27]. Besides, 4 5 carbon nanoparticles are reported to exhibit superior mechanical stretchability/ flexibility and carrier mobility, efficiently improving the anti-friction properties of the mechanical components, especially 6 for carbon nanotubes (CNT) [28, 29] and graphene [30, 31]. Kaleli and Demirtas [32] studied the 7 tribological properties of a synthetic engine with the incorporation of redox graphene oxide. The results 8 9 showed that the utilization of the redox graphite oxide minimized the friction coefficient of the ball on the polished cylinder liner by 3.29%. Moreover, carbon-based nanomaterials simultaneously benefited 10 the combustion progress and the tribological characteristics, which is of great significance in the 11 12 improvement of fuel economy. Chacko and Jeyaseelan [21] studied the influence of graphene-based fuel additives upon the combustion and emission behavior in a turbocharged diesel engine, where a 13 decrement of 5.5% in BSFC and an increment of 1.4% over brake thermal efficiency (BTE) were 14 15 observed. Similarly, within our prior investigation, graphene oxide and CNTs led to considerable fuel utilization enhancement upon incorporation into the methanol/diesel blends, with BSFC reduced by 16 1.7% and BTE increased by 4.8% [33]. In the study conducted by Selvan et al. [34] focused on the 17 characteristics of the engine fueled in diesel-ethanol-biodiesel blends adding nano-additives 18 containing a combination of cerium oxide nanoparticles and CNT. The results of the study pointed out 19 that the combined effect of CNT and cerium oxide resulted in enhanced fuel economy, accompanied 20 by a 7.7% decrease on BSFC and a 7.5% increase on BTE. What's more, many studies have focused 21 on the comparative analysis of carbon nanomaterials and metal nanomaterials, where the relative 22

prominence of carbon nanomaterials for abatement is revealed. Ooi et al. [35] conducted a comparative 1 study for single-walled carbon nanotubes, cerium oxide and graphene oxide, discovering that single-2 3 walled carbon nanotubes provided maximum benefits in terms of combustion and emissions, along with reductions of 10.3%, 14.6%, 23.4% and 24.1% in ignition delay, combustion duration and CO, 4 5 HC emissions, respectively. The impacts of carbon nanoparticles and Ag nanoparticles on the combustion parameters of the engine were investigated comparatively in the study conducted by Najafi 6 [36]. Compared with the nanofuels with Ag nanoparticles, the nanofuels with CNT offered lower 7 BSFC and CO emissions, yet marginally higher HC emissions. In the study conducted by Mei et al. 8 9 [37], CNT has demonstrated a more pronounced improvement in ignition quality and emission reduction (HC, CO, smoke, NOx) in comparison with MoO<sub>3</sub>. Maniganda et al. [38] explored the effect 10 of TiO<sub>2</sub>, CNT, Al<sub>2</sub>O<sub>3</sub>, CuO, CeO<sub>2</sub> and hydrogen blends on the combustion, performance and emission 11 12 characteristics of the dual-fuel engine. The maximum reduction in CO was achieved by TiO<sub>2</sub>, while the minimum emissions in HC and NOx were obtained for CNT, with decrements of 90% and 33%, 13 respectively. It can be seen that compared to metallic nanomaterials, although it is debatable whether 14 carbon nanomaterials possess absolutely more outstanding capability in emission reduction, carbon 15 nanomaterials are firmly proven to cause minor NOx discharge, which is definitely conducive to the 16 mitigation of environmental pollution issues. In addition, carbon-based nanomaterials are 17 acknowledged to offer significant industrial enhancements, including removing dyes from wastewater 18 [39], improving the performance of epoxy composites [40] and modifying glassy carbon electrodes 19 [41]. These industrial requirements have stimulated continuous technological renewal in the 20 manufacturing of carbon-based nanomaterials. Though their price is currently high due to the 21 complications in the production process [42], there is a tendency for it to diminish over time, and 22

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carbon nanomaterials are expected to be more of a cost-effective alternative to costly metallic materials and thus are more likely to be widely used as fuel additives in the future.

3 Ethanol, as a renewable diesel substitution, is capable of reducing in-cylinder incomplete combustion and soot emissions, whereas the high latent heat value (LHV) and low calorific value of 4 5 ethanol have also set restrictions on its extensive use. Carbon nanomaterials, featuring their superior environmental benefits over metallic nanoparticles, along with favorable fuel-burn nature, are believed 6 to complement the cooling effect and low fuel energy content of ethanol, while offering further 7 improvement in fuel economy without penalty in terms of harmful emissions. Furthermore, carbon-8 9 based nanomaterials and ethanol, served as renewable materials, could be produced from renewable resources by pyrolysis and alcoholic fermentation, respectively, and offer high environmental benefits 10 as a novel renewable fuel additive upon combination with each other. However, the present 11 12 mechanisms of this new renewable fuel additive contributing to combustion improvement and abatement effect remain immature, thus in-depth studies on the joint impact of carbon-based 13 nanoparticles and ethanol against combustion, performance and emission of the engine is especially 14 critical. This paper focuses on the influence of incorporations of three sorts of carbon nanomaterials 15 (graphene oxides, multi-layered graphene oxides and multi-walled carbon nanotubes) towards the 16 combustion and emission characteristics in the engine fueled with the diesel/ethanol blended fuel to 17 investigate the co-mechanism of ethanol and carbon nanoparticles. The goals of this study are listed 18 below. 19

20 1) Comparative analysis of the impacts of diverse carbon nanoparticles on combustion behavior21 and emissions.

22

2) Selection of the optimal carbon nanomaterial, nanoparticle concentration and loading

1 conditions.

2 3) Evaluation of the joint effect of ethanol and carbon nanoparticles on combustion and
3 emissions characteristics of the engine.

## 4 2. Materials and methods

#### 5 2.1. Fuel preparation

The fuels employed in this experiment include diesel, the diesel/ethanol blended fuel and the 6 diesel/ethanol nanofluid fuel. The pure diesel fuel is denoted by D100. The diesel/ethanol blended fuel 7 containing 85 vol% diesel and 15 vol% ethanol is referred to as E15. The diesel/ethanol nanofluid fuel 8 9 was obtained by adding carbon nanoparticles (CNPs) to the E15 fuel, and it varies in terms of the types (graphene oxides GO, the multi-layered graphene oxides MGO and the multi-walled carbon nanotubes 10 MWCNT) and the dosages (25ppm, 100ppm) of CNPs addition. For example, the diesel/ethanol 11 12 nanofluid fuel with the graphene oxide (GO) added in a dosage of 25ppm into the E15 fuel was shorted as EGO25. Similarly, the EMGO25 is the E15 fuel with muti-layered graphene oxides (MGO) in 13 25ppm. The E15 fuel with multi-walled carbon nanotube nanoparticles in a mass fraction of 100ppm 14 was EMWCNT100. The primary properties of CNPs and the physiochemical properties of tested fuels 15 are shown in Table 1 and Table 2, respectively. For the preparation for the diesel/ethanol nanofluids, 16 the ethanol was blended with 2000ppm surfactant triton-X100 (Sigma Aldrich, cat#93426-100mL), 17 and the nanoparticles were incorporated in the mixing process. Afterward, the resulting ethanol 18 nanofluids were added to diesel as fuel additives to obtain the diesel/ethanol nanofluids. The whole 19 process was conducted under the powerful stirring of an electromagnetic mixer (at 3000rev/min for 30 20 min), followed by an ultrasonication for 30 minutes to prevent the agglomeration of CNPs. 21

22 Table 1. The carbon nanoparticle additives specifications

Chemical name	Graphene oxides	Multi-layered graphene oxides	Muti-wall carbon nanotubes	
Appearance (color)	Black brown	Black	Black	
Purity (%)	95	95	>95	
Specific area $(m^2 \cdot g^{-1})$	5~200	5~150	230~270	
The diameter (nm)	1	3.4~8	3~15	
The length(µm)	10~50	5~50	3~12	
Number of polies	1~2	5~10	8~15	
Oxygen content (%)	~45	~8	~0	
Thermal conductivity	5000	~3000	3000	

1 Table 2. Physiochemical properties of tested fuels

Properties	D100	Ethan ol	EGO25	EGO100	EMGO25	EMGO100	ECNT25	ECNT100
Density (kg/m <sup>3</sup> @15°C)	830	803	826.4	827.8	827.3	828.9	827.7	829.5
Viscosity (mm <sup>2</sup> /s@40°C)	3.35	1.08	4.016	4.049	4.014	4.047	4.01	4.040
Latent heating value (LHV, kJ/kg)	260	900						
Cetane number	50.2	9	46.6	48.4	44.7	47.6	47.1	49.0
Calorific value (MJ/ kg)	42.8	27	41.08	41.44	41.16	41.24	41.12	41.65

# 2 2.2. The experimental engine test

Tests were performed on a single-cylinder, four-stroke, water-cooled CI engine with the 3 specifications listed in Table 3. The engine test bench is presented in Fig.1. The engine tests were 4 conducted under a fixed speed of 1200 rpm over a broad range of engine loads, i.e., low (10% and 5 30%), medium (50%), and high (70% and 90%) loads, correlating to torques of 5, 15, 25, 35, and 45 6 7 N m, respectively. During testing, the timing and pressure of the injection were maintained at  $18^{\circ}$ before the top dead center (BTDC) and 18MPa, respectively. An eddy current dynamometer (Shenck 8 CW25) is attached to the engine, while a dynamometer controller (MIKE (LUOYAN) HORIZON, 9 CMU3A) is engaged to manage the torque and speed of the engine. In the experiment, the fuel 10 consumption was measured by the flowmeter (Shanghai Diesel Engine Research, FCM-D). The 11 cylinder pressure sensor (AVL GH14D) mounted on the head of the cylinder was employed to obtain 12 the signal related to cylinder pressure. Subsequently, the combustion analyzer (AVL HR-CA-B1) 13

processed the signal and calculated the instantaneous heat release rate [43]. To minimize the impact of 1 inter-cycle variations, 150 consecutive in-cylinder pressure cycles were employed for the combustion 2 3 evaluation. The investigation focuses on the emissions of hydrocarbon (HC), nitrogen oxide (NO<sub>X</sub>), carbon monoxide (CO) and soot. The first three measurements were performed with a gas analyzer 4 (MEXA-584L, HORIBA) whilst the last one was conducted in an opaque smoke meter (Dismoke 4000, 5 AVL). To ensure the accuracy of the experiment, the calibration of the instruments was carried out 6 before measurements. The resolution and accuracy above experimental apparatus are displayed in 7 **Table 4**. The total experimental error  $\theta_{Exp}$  can be estimated to be 0.54% by the method as follows [44]: 8

$$\theta_{Exp} = \sqrt{\theta_{speed}^2 + \theta_{torque}^2 + \theta_{pressure}^2 + \theta_{CO}^2 + \theta_{HC}^2 + \theta_{NOx}^2 + \theta_{smoke}^2}$$

For the formula above, θ<sub>x</sub> represents the uncertainty in the measurement of the experimental data
 x given in Table 2. To guarantee a reliable and accurate result of the experimental emissions, all
 parameters were measured three times under the same conditions to obtain the average value.

Before each test, the preparation of new fuel was just completed. Prior to each fuel renewal, the 13 engine would operate with the new fuel for a period of time until no noticeable fluctuations occurred 14 in engine loads or emissions. Throughout the test period, the temperature of the coolant and the oil 15 were maintained within the range of  $80 \pm 5^{\circ}$  and  $90 \pm 5^{\circ}$  respectively so as to secure the replicability 16 and comparability of the experiments. Otherwise, monitors of discharge temperatures and lubrication 17 pressures are performed on the testing engine to assure normal operation in the engine. Upon 18 completion of the experiment, the check for residue was conducted inside the fuel tank and pipeline, 19 and no left for nanoparticles was observed. 20

21 **Table 3**. Specifications of the testing engine

Engine specifications Engine type Bore× Stoke

Single cylinder 4-stroke 100mm×115mm

Compression ratio	17.5
Displacement	0.903L
Rated power/speed	12.1 kW/2200 rpm
Maximum toque/speed	58.3 N · m /1760 rpm
Injection nozzle	0.32 mm/4
Nozzle opening pressure	18 MPa
Fuel injection advance	18±1 °CA
Cooling type Valve phase Intake valve open Intake valve closed Exhaust valve open Exhaust valve closed	Water-cooled 12 ° CA before TDC 38 ° CA after BDC 55 ° CA before BDC 12 ° CA after TDC

**1 Table 4**. Revolution values and accuracy of apparatus

Measurement apparatuses	Resolution	Uncertainties
Dynamometer		
Torque measurement	0.01 N·m	$\pm 0.2\%$
Speed measurement	1 rpm	$\pm 0.4\%$
Cylinder pressure sensor		
Pressure transducer	0.01 MPa	$\pm 0.22\%$
Gas analyzer		
CO measurement	0.01%	<0.1%
NOx measurement	1ppm	<0.1%
THC measurement	2 ppm	<0.1%
Smoke opacity meter		
Smoke Opacity	0.1%	<0.1%



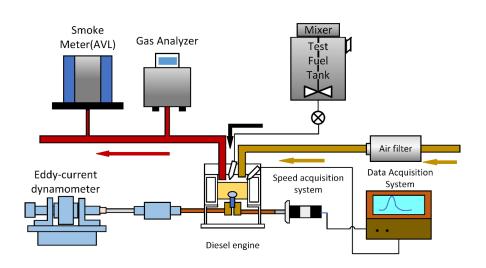
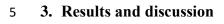


Fig. 1. The work bench of the testing engine



- 6 3.1. *Combustion characteristics*
- 7 3.1.1. Cylinder gas pressure and heat release rate

Cylinder gas pressure (CGP) and heat release rate (HRR) are the parameters that indicate the 1 combustion behavior, thereby affecting performance and emission behavior in the diesel engine. In the 2 3 same operating condition, all the tested fuels tend to have the similar trend on the curves of the CGP and HRR against crank angle, while the fuel additives cause measurable impacts on peak CGP and 4 5 peak HRR, as shown in Fig.2, for example. This indicates that the overall combustion quality and premixed combustion quantity, responded to the parameters peak CGP and peak HRR, respectively 6 [45], have been changed due to the presence of fuel additives. The variations in peak CGP and HRR 7 for all fuels with various loading conditions are depicted in Fig.3 (a) and (b). 8

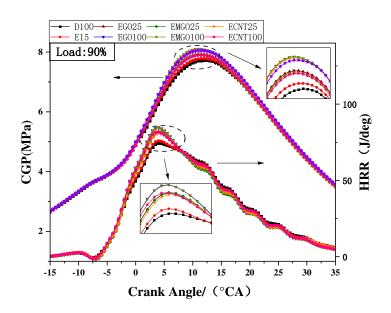
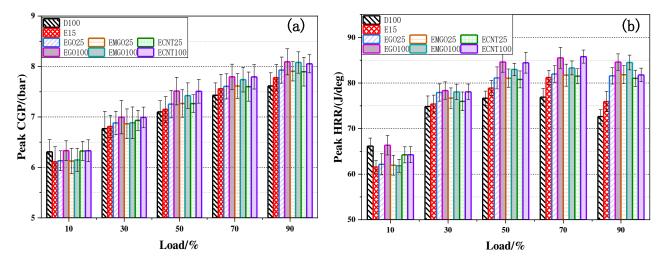


Fig. 2. The diagrams for CGP and HRR against crank angle at 90% of full load



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Fig. 3. The diagrams of (a) peak CGP and (b) peak HRR under different loads for all tested fuels.

Fig.3 (a) and (b) depict the variations in peak CGP and HRR for all fuels with various loading 2 conditions. As seen in the figure, after adding the ethanol to diesel, the peak CGP and HRR were 3 decreased at low loads, with a decrement of 3.14% and 6.95% at peak CGP and HRR, respectively. 4 This could be owing to the high latent heat of vaporization (LHV) of ethanol, which caused a drop in 5 cylinder temperature by absorbing a large amount of heat during fuel evaporation under low loads [46]. 6 Furthermore, the blending of ethanol brings about a reduction in cetane number, making it a difficult 7 condition for the ignition of fuel mixture [11]. However, as the load increased, the cooling effect of 8 ethanol was suppressed due to the increased temperature, while the low viscosity and density of ethanol 9 contributed to the well distribution of fuel and the oxygenated nature effectively alleviated the hypoxia 10 phenomenon during combustion, especially at high loads [47, 48]. Therefore, it can be observed a 11 higher peak CGP and HRR for the diesel/ethanol blend compared with diesel, with the maximum 12 increments of 2.16% at peak CGP and 4.52% at peak HRR obtained at 90% load (the largest loading 13 condition). 14

As observed, for the fuels added with CNPs, i.e. the graphene oxides (GO), the multi-layered graphene oxides (MGO), multi-walled nanotubes (MWCNT), peak CGP and HRR are significantly

1	higher compared with the diesel/ethanol blend. This is due to the high thermal conductivity and broad
2	specific surface area of CNPs, which enhanced heat transfer and the fuel spray atomization
3	characteristics, leading to a thorough combustion [37, 49]. Furthermore, the surface of CNPs possesses
4	a high activity for energy reactions, which would get pronounced under the high temperature due to
5	more reaction heat provided. This may explain why the maximum increment for CNPs addition is
6	obtained at 90% load. Additionally, with more CNPs added, peak CGP and HRR shows an ascending
7	trend. This is probably attributed to the significant heat sink effect associated with the high
8	concentration of CNPs, which facilitated the heat transfer [50]. According to the results, the peak CGP
9	and HRR increased by 5.08%, 11.4% for EGO100, 3.87%, 11.29% for EMGO100 and 3.52%, 7.69%
10	for EMWCNT100 compared with the diesel/ethanol blend, respectively. It is obvious that the GO
11	possesses the most pronounced improvement for peak CGP and HRR, followed by MGO and MWCNT.
12	The better capability in improving the peak CGP and HRR for GO towards MGO is mainly owing to
13	the fewer layers and smaller size of GO, which brought about a larger specific area and higher fuel
14	oxidation efficiency [51]. The higher peak CGP and HRR for fuels with MGO over that of MWCNT
15	is attributed to the oxygen functional groups of MGO, which increased the combustion rate [21]. This
16	trend is consistent with the similar experiment carried out by Ma et al. [33], who found the
17	improvements on peak CGP and HRR after doping GO nanopowder into the blended fuel (methanol
18	in 10% and diesel in 90%). In detail, they reported that the addition GO elevated the peak CGP and
19	HRR by 5.8% and 13%, respectively, which is higher than the results of this experiment. This is
20	probably because the inclusion of 10% methanol is considered to be able to achieve a smaller viscosity
21	for the fuel compared to 15% ethanol substitution, which reduced the droplet size and increased the
22	fuel-air contact area, favorable for the heat transfer and catalytic effect of the CNPs. In comparison to

diesel, the combined effect of ethanol and CNPs enhances cylinder combustion slightly at low loads,
 yet considerably at high loads, with maximum enhancements of 6.29% and 16.45% in peak HRR and
 CGP for EGO100, respectively.

## 4 3.1.2 Ignition delay and combustion duration

The ignition delay (ID) for all fuels with a wide range of loading conditions is demonstrated in **Fig.4 (a)**. The ignition delay represents the crank angle period between the start of fuel injection and arrival at 10% burned mass fraction, including two periods i.e. the physical delay period and the chemical delay period, which are influenced by the evaporation and cetane number of the fuel,

9 respectively [52, 53].

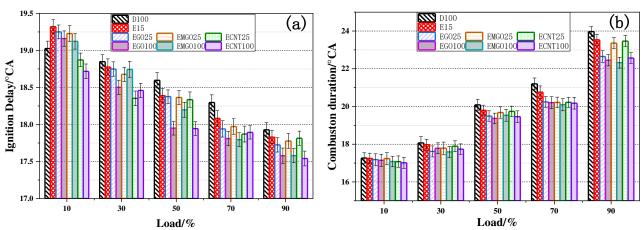




Fig. 4. The diagrams of (a) ID and (b) CD under different loads for all tested fuels.

In the figure, ID presents a decreasing trend with increasing load, which is because the evaporation of fuel droplets was facilized by the higher temperature at higher loads. The diesel/ethanol blend is observed to have a prolonged ID at low loads and a shortened ID at high loads compared with diesel. This is attributed to the high LHV and low cetane number that come with ethanol, which lowered the cylinder temperature, resulting in a retarded initiation of combustion [11]. However, the cooling effect of ethanol is chipped under higher temperature at higher loads, while the droplet size reduction and oxygen content associated with ethanol significantly shortened the physical and chemical delay period

[47, 54], resulting in a decrement in ID at high loads. As shown, the diesel/ethanol nanofluid presents 1 a shortened ID relative to the diesel/ethanol blend under most conditions. The high thermal 2 3 conductivity and surface-to-volume ratio of CNPs are responsible for this, as these properties enhance the evaporation rate of fuel droplets and heat transfer between fuel droplets and nanoparticles [49, 55], 4 5 especially under a high dosage of nanoparticles. The greatest improvement in ID is obtained at 10% load, as CNPs addition could improve the evaporation of fuel droplets by absorbing heat from radiation, 6 therefore lowering the temperature required for auto-ignition [35]. Among all CNPs, as calculated, 7 MWCNT addition has the most pronounced effect on shortening ID, with a reduction by 3.12%, 8 9 followed by GO and MGO. It can be attributed to its highest improvement for cetane number (see Table 2) and the largest surface area (see Table 1) with defect bits attached [37], which had a relatively 10 pronounced effect on accelerating the chemical delay period. In comparison with MGO, GO possesses 11 higher thermal diffusivity due to its smaller size (see Table 1), thus facilitating the heat transfer and 12 ignition process [56]. Moreover, although GO and MGO show less advantageous in shortening the ID 13 towards MWCNT, they are reported to have a good performance advancing the combustion through 14 special exothermic reactions, which easily occurred under low temperatures, according to the work 15 conducted by Ooi et al. [57]. 16

The combustion duration (CD) for all fuels with a wide range of loading conditions is demonstrated in **Fig.4 (b)**. The combustion duration is usually considered as the crank angle at which the burned mass fraction ranges from 10% to 90%. In the figure, it shows an upward trend of CD with the increasing load, which is due to more time needed to burn more injected fuel. Meanwhile, a shorter CD of the diesel/ethanol blend with respect to diesel is observed. It is because the combustion is accelerated due to the well-distributed air-fuel mixing, which could be attributed to the low viscosity,

boiling point and density of ethanol [48, 58]. Furthermore, the oxygen content of ethanol could 1 alleviate the hypoxia phenomenon during the diffusive combustion [59], especially for high loads, 2 3 where a larger proportion of diffusion combustion occurs. As in Fig.4 (b), with CNPs added to the diesel/ethanol blend, the CD is reduced generally. The main reason for this is that the high thermal 4 5 conductivity of CNPs improved the heat transfer rate [22, 55], meanwhile, the high catalytic activity accelerated the combustion reactions [60]. Towards increased load and the nanoparticle dosage, CD 6 shows a decrement trend broadly, indicating that the catalytic effect was enhanced as more catalytic 7 sites and reaction heat were provided, respectively. By calculated, GO performs the best in facilitating 8 9 the combustion process, with CD decreased by 4.59%, followed by MGO and MWCNT. Compared with MGO, GO possesses a smaller size and higher thermal conductivity, which means a better 10 enhancement for fuel oxidation and heat transfer [21, 61]. The shorter CD for fuels with MGO over 11 12 MWCNT is mainly because of the inbuilt oxygen of MGO, which promotes the combustion process [22]. 13

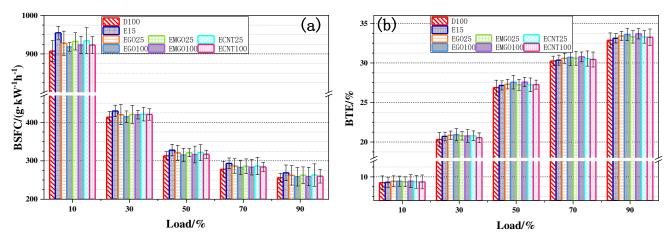
Compared with D100, the joint effect of ethanol and CNPs optimizes the combustion process, 14 with the ID and CD decreased by 2.63%, 2.64% at low loads and 2.74%, 6.86% at high loads, 15 respectively. However, this seems unremarkable in comparison to that of the metal-based nanoparticles. 16 According to previous studies, the decrements of 2.9%, 11% and 26% in ID were found after adding 17 alumina [11], titanium dioxide [62] and copper oxide [63], respectively, while the CD reductions of 18 9.2% [11], 7.7% [64] were achieved by the inclusions of cerium oxide and alumina, respectively. In 19 contrast, the inferior performance towards the combustion process improvement for CNPs is probably 20 21 attributed to the relatively smaller thermal conductivity and faster degradation rate of carbon-based materials [21, 42]. Nevertheless, it is the rapid decomposition of carbon-based materials during 22

1 combustion that results in few residuals of CNPs in the cylinder, therefore compared with metal-based

2 nanoparticles, the long-term operation with CNPs may have less impact on the engine construction.

# 3 3.2. Brake specific fuel consumption and Brake thermal efficiency

Brake specific fuel consumption (BSFC) is the amount of fuel consumed per kilowatt hour, while
the brake thermal efficiency (BTE) defined as the ratio of the power output to the heat equivalent of
the burned fuel, which represents the capability to utilize fuel energy. The variations of BSFC and BTE
for each tested fuel under various loads are depicted in Fig.5 (a) and (b), respectively.



8



As in the figure, an increasing trend in BSFC and a decreasing trend in BTE with the growth of 9 load could be observed. This is because the higher temperature of higher loads could promote more 10 complete combustion [65], thus the combustion efficiency got elevated and less fuel is consumed. 11 Compared with diesel, the diesel/ethanol blend exhibits a higher BSFC, as the inclusion of ethanol 12 lowered the calorific value, causing more amount of fuel required to reach the same load [8], especially 13 at high loads, with a maximum increase of 5.48%. However, the blending of ethanol into diesel is 14 15 observed to present an increment in BTE. It is related to the low density, viscosity and oxygenated nature of ethanol, which improved the combustion characteristics and energy content for fuel [66, 67]. 16 Moreover, the low cetane number associated with ethanol expands the proportion of premixed 17

1 combustion, where a better combustion efficiency is reached [68].

In Fig.5 (a) and (b), the diesel/ethanol nanofluids depicts lower BSFC and higher BTE compared 2 3 with the diesel/ethanol blend. The main reason should be attributed to the violent and rapid droplet breakup associated with the presence of CNPs and ethanol, known as 'micro-explosion', which is 4 5 favorable for the evaporation and distribution of fuel, in turn enhancing the catalytic activity for CNPs [69, 70]. Therefore, the dispersing of CNPs elevated the density of air-fuel charge and improved the 6 combustion quality [71], especially for low loads, with BSFC decreased by 3.8% and BTE increased 7 by 1.5%. With more CNPs added, both the decrement in BSFC and the increment in BTE are more 8 9 apparent, indicating a pronounced improvement in the catalytic effect of CNPs. As calculated, GO, MGO and MWCNT decrease the BSFC at ranges of 2.1%-3.8%, 2.0%-3.8%, 1.9%-3.2% and increase 10 the BTE at ranges of 0.6%-1.5%, 0.3%-1.7%, 0.3%-0.8%, respectively. Obviously, the improvements 11 12 for GO and MGO are comparable, whereas that for MWCNT is the minimum. It is because the oxygenated functional groups within MGO and GO, which were released during combustion, resulted 13 in an elevation in fuel energy content [70]. Compared to D100, the joint effect of CNPs and ethanol 14 15 has caused slightly higher BSFC but significantly increased BTE. Moreover, the more CNPs added, the more pronounced it presented. When adding ethanol and GO in 100ppm, the optimum 16 improvement in BTE is achieved, ranging in 1.54%-3.02%, only with a little compensation in BSFC, 17 ranging in 0.26%-1.72%. This indicates that under the combined effect of ethanol and CNPs, the 18 engine possesses the better capability to utilize the energy in the fuel, in other words, a better fuel 19 economic performance. 20

21 3.3. *Emission characteristics* 

22 3.3.1. Carbon monoxides

The emission of carbon monoxide is aroused from the nonuniform air-fuel mixing, the incomplete
 combustion and inadequate oxidation [72]. The brake specific emission levels of carbon monoxide
 (BSCO) emissions for all tested fuels at different loading conditions are shown in Fig.6.

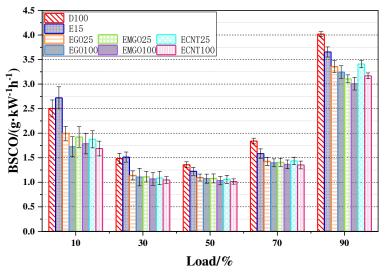


Fig. 6. Measurements of brake specific carbon monoxide emissions under different loads for all tested fuels 4 5 In the figure, it is observed a downward trend followed by an upward trend as the load increases, where the minimum BSCO is reached at 50% load. The decrease in BSCO at 10%-50% load is owing 6 to the elevated temperature under increased load, resulting in the complete combustion, while the 7 increase at 50%-90% load is due to the significantly lowered air-fuel ratio with increased load, which 8 hindered the oxidation for fuel. From the graph, it can be observed that compared with diesel, the 9 10 diesel/ethanol blend has a higher BSCO at low loads but lower BSCO at high loads. The main reason for the increment in BSCO at low loads is that the cooling effect caused by ethanol resulted in a decline 11 in cylinder temperature, giving birth to more incomplete combustion. With the load increased, the 12 cooling effect was suppressed due to the ascended temperature, whereas the oxygen content in ethanol 13 significantly improved the oxidation in rich zones of combustion. However, this result is in contrast to 14 the finding of Rakopoulos et al. [68], who concluded that the incorporation of ethanol could minimize 15 carbon monoxide emissions at low loads. In fact, in their study, the volumetric substitution of ethanol 16

(5%) was far less than that of this article, affecting the LHV of the fuel to such a minor degree that no
cooling effect could be observed, which possibly offered a reason for the discrepancy in the result. The
results of this paper are generally concordant with those in prior studies. Zhu et al. [66] revealed that
ethanol addition in biodiesel happened to exhibit the cooling effect under light loads when volume
substitution of ethanol reaches 10%. Nevertheless, Fang et al. [73] concluded that the ethanol additive
had a minimal elevation on carbon monoxide emissions at the injection time of 7.5 ° CA before TDC,
providing a fresh method of alleviating the cooling effect brought by alcohol substitution.

In Fig.6, it can be seen that the incorporation of CNPs to the diesel/ethanol blend lowers the BSCO 8 9 detectably, especially at a high dosage of nanoparticles. This is derived from the presence of CNPs homogenized the mixing of fuel and air by promoting the formation of micro-explosion and secondary 10 atomization, then with well contact with fuel, the catalytic reactions were enhanced, leading to a 11 12 thorough fuel combustion [21, 69]. Among all CNPs, the MWCNT has the greatest improvement in reducing BSCO, with the maximum decrement of 37.95%, followed by GO and MGO. This is because 13 the highest surface-to-volume ratio of MWCNT significantly promoted the combustion reactions, 14 15 meanwhile, MWCNT acted as a CO<sub>2</sub> absorbent and inhibited any dissociation reaction of CO<sub>2</sub> [42]. The superior effect of GO compared with MGO on reducing the BSCO is because the higher thermal 16 conductivity of GO permits more heat transmitted to the particular fuel molecules, where the catalytic 17 oxidation was improved [74]. Under the joint effect of ethanol and CNPs, the BSCO presents a 18 significant decrement, particularly at low loads, with a maximum of 32.59% for ECNT100. This is 19 consistent with the results found by Ooi et al. [75], who made a comparative investigation on the 20 influences of graphene oxide, single-wall carbon nanotubes and cerium oxide nanoparticles upon the 21 emission behavior for a diesel engine. They revealed that the best optimization for reducing carbon 22

monoxide is achieved by single-wall carbon nanotubes under low loads, with a decrement of 23.4%.
Furthermore, with specific functional groups, the carbon nanoparticles were reported to cause a larger
drop in the formation of carbon monoxide, with a reduction by 37.6% for nitrogen-doped MWCNT
and 35% for amino-functionalized MWCNT [55, 76].

5 *3.3.2. Hydrocarbons* 

Fig.7 shows the brake specific hydrocarbon emissions (BSHC) for various fuels under different
loads. The main causes for the formation of hydrocarbons are insufficient to fuel evaporation, overrich or over-lean air-fuel mixture and fuel spray impingement towards the wall [77].

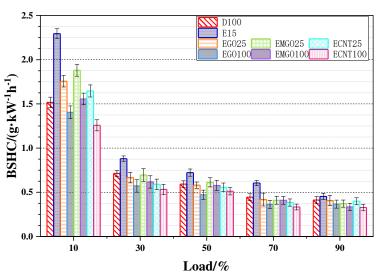


Fig. 7. Measurements of brake specific hydrocarbons emissions under different loads for all tested fuels 9 In the figure, the BSHC for all tested fuels shows a downward trend with the increasing load, 10 which is mainly caused by the incremental temperature, where complete combustion occurred more 11 easily. As observed, the BSHC for the diesel/ethanol blend is notably higher in comparison with that 12 of diesel. This is due to the leaner air-fuel mixing caused by the oxygen nature of ethanol, which is not 13 favorable for flame propagation [54, 78]. Moreover, the lower viscosity and density of ethanol may 14 lengthen the spray penetration, with more spray impingement towards the cylinder wall. These could 15 be the reasons why the inclusion of ethanol promotes the formation of hydrocarbons. At 10% load, the 16

maximum increment of 51.24% is obtained, which could be attributed to the high LHV of ethanol,
which significantly deteriorates the fuel evaporation efficiency under the low cylinder temperature at
low loads. With the load rises, the elevated temperature suppressed the cooling effect, alleviating the
increment on hydrocarbon emissions.

5 In Fig.7, the effect of adding CNPs to the diesel/ethanol blend decreases the BSHC, particularly under low loads, with a reduction by 45.18%. It is the high thermal conductivity and pronounced 6 catalytic effect of CNPs that improved the fuel evaporation quality [55, 79] and promoted the oxidation 7 of hydrocarbons [80]. Furthermore, these properties of CNPs shortened the combustion process (see 8 9 Fig.4), lessening the generation time for hydrocarbons [21, 81]. The reduction is observed to get significant with more CNPs added, indicating that a high catalytic activity is presented under a high 10 nanoparticle concentration. By contrast, the MWCNT has the greatest reduction in BSHC, with a 11 12 maximum decrease by 45.18% for ECNT100. It is associated with the highest specific area and thermal conductivity of MWCNT, which significantly optimizes the evaporation and oxidation of fuel [69]. 13 Compared with D100, the BSHC for fuel is decreased under the joint effect of CNPs and ethanol, 14 15 especially in a high dosage of nanoparticles. The optimum reduction of 25.42% in BSHC was attained with the addition of ethanol and GO at 100ppm. 16

17 *3.3.3. Nitrogen Oxides* 

Fig.8 shows the brake specific nitrogen oxides (BSNO<sub>X</sub>) emission for various fuels with different loading conditions. Generated from the chemical reactions between nitrogen and oxygen under a high temperature environment, the nitrogen oxide emission is mainly affected by the combustion temperature, local oxygen and the residence time under high temperatures.

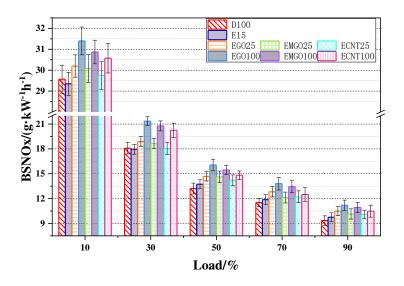


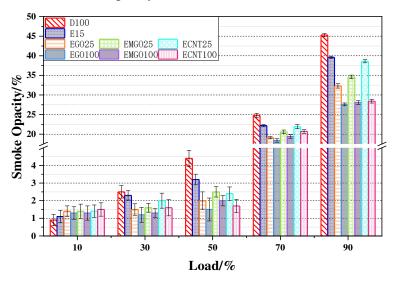
Fig. 8. Measurements of brake specific nitrogen oxides emissions under different loads for all tested fuels 1 2 As shown in the figure, as the cylinder temperature and combustion duration are elevated, the emissions of nitrogen oxide do increase with increasing load. However, the output power presents a 3 greater increase, consequently resulting in a decreasing trend in BSNO<sub>X</sub>, as shown in the figure. With 4 5 the load increases, the blending of ethanol into diesel is observed to have a notable decline at low loads and an increase at high loads. The decline at low loads is aroused from the cooling effect due to the 6 high LHV and low cetane number associated with ethanol, which reduced the temperature significantly 7 under low loads, leading to a lower BSNO<sub>X</sub>. However, the cooling effect is chipped under the higher 8 temperature of higher load, whereas the bounded oxygen of ethanol promoted oxidation of the fuel 9 10 significantly at high loads, with more nitrogen oxides formed.

As shown in **Fig.8**, the CNPs addition increases the BSNO<sub>X</sub> regardless of the loading conditions, especially for the high concentration. This is because the high thermal conductivity and large specific surface area of CNPs enhanced the complete combustion remarkably, increasing the cylinder pressure and corresponding temperature, thus a significant increment on BSNO<sub>X</sub> is obtained at high loads [82, 83]. Specifically, the oxygen functional groups in GO and MGO assisted the oxidation of nitrogen [21], implying higher BSNO<sub>X</sub> for GO and MGO relative to MWCNT.

1	Compared with D100, under the combined effect of ethanol and $\text{CNPs}$ , $\text{BSNO}_X$ is elevated by
2	5.22%-21.46%. In detail, the EGO25/EGO100, EMGO25/EMGO100, ECNT25/ECNT100 present
3	increments in the ranges of 2.14%-12.23%/6.19%-21.46%, 1.75%-10.63%/4.4%-16.95%, 0.6%-
4	7.83%/3.4%-12.11% on BSNO <sub>X</sub> , respectively. Obviously, the highest increment in nitrogen oxides
5	emission is obtained for the fuel with GO added in 100ppm. However, the increments are not apparent
6	when compared with the results from other studies. As previous research reported, the addition of
7	alumina, ceria and titanium dioxide into the fuel brought about further higher increase in emissions of
8	nitrogen oxides, which is up to 40% [44], 27.8% [84], 31.87% [85]. By contrast, increase in $BSNO_X$
9	caused by the joint effect of ethanol and CNPs is more acceptable.

10 3.3.4. Smoke opacity

11 The smoke opacity reflected the emission of soot, which mainly comes from the partial reactions 12 between carbon atoms within the fuel and the incomplete combustion of hydrocarbons. **Fig.9** 13 demonstrates the variation of smoke opacity across various fuels at different loading conditions.



14

Fig. 9. Measurements of smoke opacity under different loads for all tested fuels

In this figure, it can be observed that the smoke opacity has an increasing tendency with the rise of load. This is because with more fuel injected at a higher load, the air-fuel mixture got richer,

followed with more incomplete combustion, and then more soot was generated. Compared with diesel, 1 the smoke opacity of the diesel/ethanol blend was higher under low loads yet lower under high loads. 2 3 This is mainly driven by a reduction in cylinder temperature as a result of the high LHV associated with ethanol, which significantly resulted in more incomplete combustion under the low temperature 4 5 at low loads. However, it is suppressed at higher loading conditions for higher temperatures, whereas the oxygenated nature of ethanol promotes the oxidation in rich zones of combustion and the low 6 density, viscosity contribute to the well distribution of fuel, causing a reduction in the formation of 7 soot nuclei [73, 86]. Furthermore, the radicals of HO<sub>2</sub> and OH released from the combustion of ethanol 8 9 would consume the polycyclic aromatic hydrocarbon, suppressing the nucleation of smoke particles [87]. 10

In Fig.9, after adding CNPs into the diesel/ethanol blend, the smoke opacity for fuels is increased 11 12 at low loads and decreased at high loads. The increment at low loads is because, in the case of the short combustion duration of low loads, CNPs could not burn out in time, thus acting as soot nucleus and 13 promoting the generation of smoke particles [56]. Under high loads, with sufficient residence time to 14 burn, this phenomenon was diminished naturally, while the atomization and heat propagation of fuel 15 were significantly improved by CNPs [21, 37], inhibiting the formation of smoke particles, especially 16 towards more CNPs added. Particularly, the structural oxygen of GO and MGO released enough 17 oxygen for oxidation [22, 88], leading to the reduction in soot emissions, which may indicate the larger 18 soot emission reduction for GO and MGO compared with that for MWCNT. In detail, GO and MGO 19 contribute to the soot emission decrease in the ranges of 13.96%-47.82% and 7.2%-43.48%, and it is 20 21 obvious that GO possesses better capability in reducing soot emissions relative to MGO. This could be attributed to the higher thermal conductivity and smaller size of GO, which is conducive to fuel 22

oxidation [51]. By comparison with diesel, impacted by the joint effect of ethanol and CNPs, the smoke
opacity is reduced in ranges of 22.98%-65.91%, 16.54%-54.54%, 11.69%-61.36% for EGO100,
EMGO100, EMWCNT100, respectively. It indicates that the joint effect of ethanol and CNPs has the
collective capability to inhibit the soot emission of the diesel engine.

## 5 3.4. *Discussion on the present results*

In order to evaluate various joint effects of ethanol and CNPs with different types (GO, MGO, MWCNT) and dosages (25ppm, 100ppm),  $\Delta_x$ , a normalized parameter, is defined by Eq. (1) and listed in Table 5, which measured the maximum relative variation on the corresponding characteristic parameter at all the loading conditions raised by a specific combination of ethanol and CNPs relative to diesel fuel.

11 
$$\Delta_{x} = \max_{1 \le j \le 5} \left( \left| \frac{x_{EZi,a_{j}} - x_{D100,a_{j}}}{x_{D100,a_{j}}} \right| \right), (i = 25, 100, a_{j} = 10\%, 30\%, 50\%, 70\%, 90\%)$$
(1)

In the above equation, Z means the type of the added CNPs, including GO, MGO and CNT, while  $x_{EZi,a_j}$  and  $x_{D100,a_j}$  represent tested parameters for EZi and D100 at  $a_j$  load, respectively. "x" denotes the characteristic parameters, including peak CGP, peak HRR, ID, CD, BSFC, BTE, as well as emissions in CO, HC, NOx and smoke.

Ethanol+GO<sup>a</sup> Ethanol+MGO Ethanol+MWCNT 25ppm<sup>b</sup> 100ppm 100ppm 25ppm 100ppm 25ppm  $4.13\%_{(90\%)}^{c}\uparrow^{d}$ 5.77%(90%) ↑ 6.29%(90%) ↑ 3.82%(90%) ↑ 6.12%(90%) ↑ 3.71%(90%) ↑  $\Delta_{peak CGP}$ 12.30%(90%) 16.45%(90%) 12.65%(90%) 16.33%(90%) 11.55%(90%)↑ 12.57% (90%)  $\Delta_{peak HRR}$  $1.95\%_{(70\%)} \downarrow$ 3.47%(50%) ↓  $1.77\%_{(70\%)} \downarrow$  $2.74\%_{(70\%)}$  ] 2.63%(30%)  $3.51\%_{(50\%)} \downarrow$  $\Delta_{ID}$ 5.85%(90%) ↓ 5.51%(90%) ↓ 6.33%(90%) ↓ 4.63%(70%) ↓ 6.86%(90%) ↓ 4.62%(70%) ↓  $\Delta_{CD}$ 3.03%(70%) ↑ 1.72%(70%) ↑ 2.81%(10%) ↑ 1.96%(70%) ↑ 3.03%(70%) ↑ 2.13%(70%) ↑  $\Delta_{BSFC}$ 2.61%(30%) ↑ 3.02%(30%) ↑ 2.28%(30%) ↑ 2.63%(50%) ↑ 2.25%(30%) ↑ 1.42%(50%) ↑  $\Delta_{BTE}$ 24.99%<sub>(30%)</sub>↓ 26.74%(30%)↓ 32.59%(10%)↓  $\Delta_{CO}$ 23.16%(30%)↓ 31.09%(10%)↓ 28.69%(10%)↓ 6.68%(30%) ↓ 20.36%(50%)↓ 9.79%(90%) ↓ 18.82%(90%)↓ 17.22%(30%)↓ 25.42%(30%)↓  $\Delta_{HC}$  $12.11\%_{(50\%)}$ 12.29%(90%) 21.46%(50%) 10.63%(50%) 16.95% (50%) 7.83%(90%) ↑  $\Delta_{NOx}$ 65.91%<sub>(50%)</sub>↓ 54.55%<sub>(50%)</sub> 45.45%<sub>(50%)</sub>  $61.36\%_{(50\%)}$ 54.55%<sub>(50%)</sub>↓ 43.18%(50%)↓  $\Delta_{smoke}$ 

**Table 5**. Summary of the maximum variations raised by the combination of ethanol and CNPs.

17 Note: <sup>a</sup> Ethanol+GO means the combined additive of ethanol and GO.

1 <sup>b</sup> 25ppm represents the incorporation of CNPs at a dose of 25 ppm.

2

- <sup>c</sup> 4.13%<sub>(90%)</sub> is denoted as the maximum variation of 4.13% occurred at 90% load.
- <sup>d</sup> "↑" means that the characteristic parameter is elevated by the combination of ethanol and CNPs, while "↓"notes
   that the combination of ethanol and CNPs decreases the characteristic parameter.

5 As shown in the Table 5, driven by the combined impact of ethanol and CNPs, some characteristics of the engine are considerably optimized, involving elevations in Peak CGP, Peak HRR 6 7 and BTE, as well as drops in ID, CD and emission in CO, HC and smoke, whereas other characteristics of the engine are deteriorated, with elevated BSFC and NOx emission. Within all combinations on 8 CNPs and ethanol, the combination of ethanol and GO (100ppm) delivers the highest improvements 9 on Peak CGP, Peak HRR, CD, BTE and smoke emission, while the combination of ethanol and 10 MWCNT (100ppm) contributes to the optimal enhancements on ID and emissions in CO and HC. In 11 addition, the mildest increments on BSFC and NOx emission are accomplished by the combination of 12 ethanol and GO (100ppm) and the combination of ethanol and MWCNT (25ppm), respectively. 13 Without doubts, benefited from the oxygenated nature, the combination of ethanol and GO (100ppm) 14 greatly supplements the oxygen content of the fuel, thus dramatically boosting the combustion process, 15 fuel utilization and smoke emission minimization, especially at medium or high loads. However, with 16 the activated oxidation reaction, the combination of ethanol and GO (100ppm) equally introduced a 17 maximum growth on NOx emission. While thanks to the minimal oxygen content of MWCNT, the 18 combination of ethanol and MWCNT (25ppm) minimized NOx generation. Moreover, due to the 19 maximum specific surface area possessed by MWCNT, the combination of ethanol and MWCNT 20 (100ppm) offers a pronounced abatement effect in CO, HC and smoke emissions, especially at low 21 loads. Besides, considering that the combination of ethanol and MWCNT (100ppm) equally resulted 22 in the shortest ID, it can be inferred that certain reactions within ignition delay may be relevant to the 23 abatement mechanisms, which is particularly enhanced by the MWCNT. Therefore, with respect to 24

engine emissions control, the employment of the combination of ethanol and MWCNT (100ppm) as a
fuel additive under low loads represents a favorable choice, yet in view of the improvements in
combustion and performance characteristics of the engine, the combined fuel additive involved ethanol
and GO (100ppm) ought to be preferred for the utilization at medium or high loads.

5 4. Conclusion

This paper focuses on the impacts of three strings of renewable carbon nanoparticles (graphene
oxides, GO; the multi-layered graphene oxides, MGO; the multi-walled carbon nanotubes, MWCNT)
towards combustion, performance and emission behavior in the diesel engine under various loading
conditions at 1200rpm. Based on the findings, the main conclusions are drawn:

Inclusion of CNPs into the diesel/ethanol blend significantly benefits the combustion progress,
contributing to an increase in peak cylinder gas pressure (peak CGP) and peak heat release rate (peak
HRR), as well as a reduction in ignition delay (ID) and combustion duration (CD). The GO aroused
the most significant improvement in combustion process, followed by MGO and MWCNT.

The incorporation of CNPs in the diesel/ethanol blend could significantly improve fuel utilization with a reduced BSFC and a correspondingly increased BTE. Naturally, in contrast to pure diesel fuel, co-effects of CNPs and ethanol present an elevated BTE with only a small compensation in BSFC, especially for GO, with an increase in the ranges of 2.1%-3.8% for BTE and 0.5%-1.5% for BSFC.

The incorporation of CNPs upon the diesel/ethanol blend decreased the emissions in carbon monoxide (CO), hydrocarbon (HC) and smoke opacity, but also increased nitrogen oxides (NOx) emissions. MWCNT has the most noticeable decreasing effect on the emissions of CO and HC, while the maximum decremental effect on smoke opacity is observed for GO.

22 Different combinations of ethanol and CNPs result in differing improvements in the characteristics

of the engine. The application of the combination of ethanol and GO (100ppm) at medium and high
loads resulted in favorable improvements in the combustion process and fuel economy, whereas the
combination of ethanol and MWCNT (100ppm) caused the optimal enhancements in emission control
when operated at low loads.

5 Overall, the investigation revealed that the combination of ethanol and CNPs improved the combustion process and reduced CO, HC and soot emissions, yet NOx emissions slightly increased. 6 Considering the increase in NOx emissions, more specifically targeted studies should be developed to 7 obtain an integrated and effective emission control e.g. using other nanoparticles, employing post-8 9 treatment devices, operating with exhaust gas recirculation, etc. Further, the greatest improvement to the combustion process is obtained with GO involved, whereas the overall emission abatement effect 10 is the strongest with MWCNT incorporated, so it seems that there exists a trade-off between 11 12 combustion improvement and emission reduction. From this perspective, the authors suggest investigating the mixing of these two nanoparticles at different proportions to promote high-efficiency 13 combustion with minimal emissions. 14

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