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Full Length Article

Analysis of morphology, nanostructure, and oxidation reaction of soot particulates from CI engines with dimethoxymethane–diesel blends under different loads and speeds

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1. Introduction

Recently, the impact of aerosols on biosphere, human health, and climate change has attracted increasing research attention. Aerosols can block sunlight to plants, transmit viruses such as SARS-CoV-2, and directly cause respiratory diseases [1–3]. Particulate matters (PM) are one of the major sources of carcinogenic aerosols originating from combustion process that occur in urban and rural areas; this is a big concern [4], particularly with CI engine emissions [5] as they are considered as cancerogenic substances by the WHO in 1989 [6]. Therefore, a high-efficiency method should be proposed to solve this issue of high PM emissions of CI engines.

The development of oxygenated fuels has been triggered due to convenient maneuverability and environment protection. Oxygenated fuels have a certain oxygen fraction and a two-bit price; these characteristics make it a suitable additive for diesel fuels. Particularly, the price of petroleum has rapidly risen in recent years. Dimethoxymethane (CH\(_2\)OCH\(_2\)OCH\(_3\), DMM), as a potential alternative fuel and the smallest methoxymethylene ether, can not only be easily produced from natural gas, methanol, and coal but also has relatively high oxygen proportion (42%) and valuable high CNs (cetane number) [7]. Moreover, it is highly miscible with diesel fuel and is non-toxic [8]. It has also been stated that the emissions of soot and NO\(_X\) could be reduced simultaneously by simply accepting DMM–diesel fuels [9–11].

Due to these properties and its contribution on decreasing emissions in CI engines, a series of investigations were successfully carried out with regard to flame, ignition delay times, and detailed chemical kinetic modeling. For example, Renard et al. [12] used MBMS (molecular beam mass spectrometry) method to investigate the influence of DMM addition on species concentration profiles with premixed oxygen/ethylene/argon flame. They concluded that the DMM–diesel blends caused a slight decrease of the flame front, attributing to the replacement of...
5.7% ethene by 4.3% DMM, which shifted down the concentration of the detected intermediate species. Sinha et al. [13] measured the temperatures and species concentrations of DMM across OFDF (opposed flow diffusion flames). They found that the lack of a C–C bond in the atom structure vastly reduced the formation of acetylene, propylene, and ethylene, leading to a great reduction of soot emission. With respect to studies on ignition delay, Zhang et al. [14] performed ignition delay time for DMM–oxygen–argon mixtures at a temperature of 1103–1454 K, pressures of 2, 4, and 10 atm. They modified the parameters (reaction rate) of selected radical reactions, and concluded the fuel consumption pathway of DMM. Hu et al. [15] measured the ignition delay times of n-peptane, pure DMM, and DMM-n-heptane mixtures at a temperature of 1100–1600 K at pressures of 2 and 10 atm. They revealed enhanced chemical reactivity owing to the increasing concentration of radical pool. Thus, considerable utility in providing better insight into oxygenated hydrocarbon combustion of DMM is developed as well as matured chemical kinetic mechanisms are validated.

In front of increasingly rigorous engine emission rules and requirements, the zero-emission targets of CI engines are hardly accomplished by only accepting oxygenated fuels. The application of DPF (diesel particulate filters) is considered one of the most promising technologies for decreasing PM and other gas emissions owing to its convenience and simplicity. When an exhaust gas passes through the porous filter wall, PMs are collected and stored in the inner wall of the square channel [16]. To maintain the efficient and continuous capture ability, passive regenerations based on the catalyst would be the most widely choice to remove PM across oxidation reaction. It is found that the use of DPF achieves high efficiency of over 90% and valuable durability over distances approximately 700000 km in CI engines with diesel fuels [17]. Nevertheless, the properties of soot greatly influence oxidation during DPF regeneration procession. Here “soot” is defined as elemental carbon, but does not include ash, sulfates, and soluble organic fraction (SOF) [18]. Moreover, the soot surface chemistry and

| Table 1 | Basic parameters of the engine. |
|---------|--------------------------------|
| Engine type | Four-stroke compression ignition |
| Engine type | YC4Y22-15050 |
| Turbocharger | JEKP45 |
| Number of cylinders | 4 |
| Bore (mm) | 85 |
| Stroke (mm) | 95.6 |
| Compression ratio | 16.5 |
| Inlet valve closed (°CA ATDC) | −130 |
| Exhaust valve open (°CA ATDC) | 120 |
| Injection system | high-pressure common-rail |
| Injection pump | CRDFP3 (DELPHI) |
| Fuel injector | CRI-011 (DELPHI) |
| Electronic control unit (ECU) | DCM6.2 AP (DELPHI) |
| Maximum torque/speed (N m/rpm) | 286/1400 |

| Table 2 | Operating conditions of the engine. |
|---------|--------------------------------|
| Item | Parameters |
| Speed (rpm) Injection pressure (MPa) | 1400/2200 120 |
| Injection timing (°CA ATDC) | −3 |
| BMEP (MPa) | 0.6/1.2 |
| Intake pressure (MPa) | 0.15 |
| Intake temperature (°C) | 30 ± 1 |
| Coolant temperature (°C) | 84 ± 2 |

| Table 3 | Physical and chemical properties of blending fuels. |
|---------|--------------------------------|
| Name | Diesel | DMM | DMM6.4 | DMM13 |
| Formula | C_{10.8}H_{18.7} | CH_{3}OCH_{2}OCH_{3} | –– | –– |
| Density (g/cm³) | 0.86 | 0.865 | 0.86 | 0.862 |
| Cetane number | 45 | 30 | 44.6 | 43.1 |
| Boiling point (°C) | 188–343 | 42 | –– | –– |
| Low heating value (MJ/kg) | 42.5 | 22.4 | 41.6 | 39.9 |
| Latent heating (kJ/kg) | 260 | 318.6 | 263.1 | 268.4 |
| Kinematic viscosity (mm²/s) | 3.44 | 0.34 | –– | –– |
| Oxygen content (%) | 0 | 42.1 | 2.5 | 5 |

Fig. 1. Image of the experimental devices for soot samples.
structure could be reformed by the component of fuel content and combustion conditions \cite{19,20}. Therefore, the morphology, nanostructure, and oxidation property of soot should be understood clearly to further improve the efficiency of DPF and bring into correspondence with the introduction of oxygenated fuels, ultra-low exhaust gases can be accomplished accordingly.

Researchers have made extensive and in-depth studies on the physical properties of diesel soot, such as morphology and nanostructure. On the one hand, the morphology is connected with the combustion process. For example, Luo \cite{21} observed the morphology of in-cylinder and exhaust soot in combustion process, and observed that the morphology of in-cylinder soot is similar to that of exhaust soot, which are composed of tens, hundreds, thousands or even tens of thousands of primary particles (the individual that makes up the soot), and their shapes are quite complex. In 1975, the concept of “Fractals” was first proposed by Professor Mandelbrot of Harvard University, whose work “Fractals: form, chance and dimension.” heralded the beginning of the

Fig. 2. Aggregates morphology distribution of different fuels with 0.6 MPa and 1.2 MPa.

Fig. 3. Aggregates morphology distribution of different fuels with 1400 rpm and 2200 rpm.

Fig. 4. Soot curves of different fuels under different conditions.
formation of fractal theory [22]. To distinguish the characteristics of different soot morphologies, the fractal theory was applied to the soot of diesel engines. Transmission electron microscopy (TEM) images are usually used to analyze the morphology of exhaust soot. Dong [23] used TEM and observed that the fractal dimension of the typical in-cylinder soot of diesel fuels is between 1.2 and 1.74, and its changes first increase, then decrease, and ultimately increase in the combustion process. In other words, the geometric structure of the soot has gone through an evolution process from “compact” to “loose” and to “compact”.

On the other hand, the morphology and nanostructure are also related to the operation conditions, such as load, rotational speed, among others. For example, Lapuerta et al. [24] observed that the primary particles (the individual that makes up the soot) diameter increased with an increase in air-fuel ratio and rotational speed, while the effect of EGR rate on the diameter of primary particles was negligible. They also found that the fractal dimension of soot increased with an increase in engine load and was less affected by engine speed. Neer et al. [25] found that the primary particle diameter and the size of agglomerated particles under different speed and load increased with an increase in the ratio of burning air to space under operating conditions. Meanwhile, the size of agglomerated particles also increased with the increase in exhaust gas temperature. However, Lee [26] and Xu et al. [27] also found through experimental studies that with an increase in engine load, the particle size of primary particles gradually decreases.

To understand the changes of soot and primary particles more fully with different conditions and fuels, Ishiguro et al. [28] used TEM to study the nanostructure of primary particles under different working conditions of direct-injection diesel engines. The results show that the primary particles of diesel particulate are composed of the core and shell, regardless of the operation of the diesel. The core sits at the center of the primary particles, approximately 10 nm in diameter, and comprises many ultratine particles of 3–4 nm, on which are distributed many disordered carbon layers. The shell is composed of many concentric layers of microcrystalline carbon. With developments in technology, the nanostructure of primary particles can be analyzed using three parameters such as fringe tortuosity, fringe length, and fringe separation distance [18,29,30]. Vander Wal et al. [31] found that the nanostructure of primary particles mainly depends on the combustion environment (formation conditions), such as temperature and residence time. Zhu [32] and Lee et al. [26] found that the spacing between the microcrystalline layers of the primary particles was smaller and larger in size when the load was larger, whereas the nanostructure of the primary particles was more similar to that of graphite. In addition, Zhu et al. [32] found that the size of primary particles was small under the condition of high exhaust gas temperature, and believed that the high-temperature combustion conditions in the cylinder accelerated the oxidation of primary particles. Moreover, studies [33] have shown that the morphology characteristics of the particles have an important relation with their formation process and oxidation conditions that can be used as a key reference for evaluating the harm of the particles to the environment and human health. Müller et al. [34] and Su et al. [35] using a thermal gravimetric analyzer (TGA) on the oxidation characteristics of engine exhaust particulate inquiry found that the primary particles of nanostructure and oxidation activity and particle surface oxygenated functional groups have inseparable relations and that the graphite-particle microchip layer are packed more neatly, the less-oxygenated-functional groups on the surface of particles showed a lower oxidation activity. Yehliu et al. [19] compared the oxidation of microcrystalline structure and their activity analysis of soot between diesel and biological diesel. They found the primary particles of reaction rate constant and crystallite size demonstrate an approximate linear relation, and the primary particles surface oxygen content in discrete distribution. It can thus be concluded that the nanostructure of primary particles (crystallite size) decided to primary particles of active carbon, while oxygen or oxygenated-functional groups on the surface of the particles have a relatively small effect on the activity of particles. However, to the best of our knowledge, little research has been conducted on the influences of DMM-diesel blends on the production of inception and precursors of soot, especially the relation between oxidation, morphology, and nanostructure. To classify the regulations between nanostructure and activity (oxidation) of mature soot more fully in this context, a TEM and a TGA were introduced to acquire TEM images and conduct temperature-programmed-oxidation (TPO) experiments, respectively. The details are stated in the next section. To study the influence of DMM-diesel blends on soot oxidation, morphology, and nanostructure, tests are conducted at different rotational speeds (1400 rpm and 2200 rpm) and two loads (0.6 MPa and 1.2 MPa) with three fuels (D100, DMM6.4, and DMM13). The result of the investigation is worthy to avail the applicability of alternative fuel DMM

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**Table 4**

| Fuels | Operation conditions | Air-fuel ratios | Lambda (λ) | Exhaust Gas Temperature (°C) |
|-------|----------------------|----------------|------------|-----------------------------|
| D100  | 1400 rpm-0.6Mpa      | 32.76          | 2.25       | 208                         |
|       | 1400 rpm-1.2Mpa      | 20.43          | 1.4        | 313                         |
|       | 2200 rpm-0.6Mpa      | 35.73          | 2.45       | 253                         |
|       | 2200 rpm-1.2Mpa      | 20.6           | 1.41       | 363                         |
| DMM6.4| 1400 rpm-0.6Mpa      | 33.13          | 2.27       | 233                         |
|       | 1400 rpm-1.2Mpa      | 20.43          | 1.39       | 340                         |
|       | 2200 rpm-0.6Mpa      | 35.46          | 2.41       | 248                         |
|       | 2200 rpm-1.2Mpa      | 19.7           | 1.35       | 413                         |
| DMM13 | 1400 rpm-0.6Mpa      | 33.2           | 2.27       | 233                         |
|       | 1400 rpm-1.2Mpa      | 19.8           | 1.36       | 337                         |
|       | 2200 rpm-0.6Mpa      | 35.46          | 2.41       | 239                         |
|       | 2200 rpm-1.2Mpa      | 19.7           | 1.35       | 407                         |

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![Fig. 5. Aggregates fractal dimension (Df) with different fuels in different conditions.](image-url)
on further decreasing exhaust emissions, improving the recognition of particulates, and accomplishing the emission rules of CI engines.

2. Test apparatus and methods

2.1. Test engines

The experiment is conducted using a turbocharged, four-cylinder engine with a high-pressure common-rail in-cylinder injection system. The specific parameters are shown in Table 1. The detailed image of experimental devices for soot sample displays are as shown in Fig. 1. During the experiment, a PowerLink eddy-current dynamometer is used to maintain the engine speed in the range of 1400 rpm and 2200 rpm. A Kisler 6052CU20 is used to measure in-cylinder pressure. Within the test duration, the inlet air pressure is kept to 0.15 MPa, the inlet air temperature is kept at 30 °C, and the oil and cooling water temperature are kept at 84 ± 2 °C, more detail are shown in Table 2. For each fuel, cylinder pressures from 100 cycles were acquired and averaged.

Fig. 6. The diameter distribution of primary particles (dp) of different fuels.
2.2. Fuel properties

In this experiment, different test fuels are used, and the physical and chemical properties of DMM and diesel are shown in Table 3. The proportion of fuels is diesel (D100), diesel with 6.4% (v/v) DMM (DMM6.4) and a 13% (v/v) DMM (DMM13).

2.3. Soot sample collection and analysis

2.3.1. TEM analysis

Soot morphology and nanostructure are originate from the TEM images that are collected using a HRTEM (high-resolution transmission electron microscope), Philips Tecnai F20, by 0.248 nm point resolutions at 200 kV. A MBSM (momentum-based sampling method) is introduced to collect soot sample before using TEM equipment. Exhaust gases, which come from exhaust pipeline in CI engines, are forced to the TEM grids using a vacuum pump. PM samples subside on high TEM grids. Afterwards, the soot samples are uninterruptedly flushed by dichloromethane solvent, and obtain the experimental samples. Same processes of fringe analysis and digitization of TEM images are referred from paper of previous studies [29,36].

2.3.2. Oxidation analysis

The soot samples from exhaust gases are first collected on the Teflon filters. In this time, many unburned organic matter would be adsorbed on the surface of the soot particles, which will bring errors to the nanostructure and oxidation analysis. Therefore, the sample has to be extracted before the analysis to eliminate the interference of organic components. Therefore, the ultrasonic bath method is adopted. The samples are soaked in dichloromethane, and the ultrasonic bath is used to separate the organic components by means of vibration, then dried in a drying oven at 50 °C for 30 min. Finally, samples are taken out and placed in petri dishes, and the petri dishes placed in a dryer for preservation.

A TPO experiment is conducted to explore soot oxidation reaction by a TGA, Mettler-Toledo TGA/DSC1 that equips platinum crucibles. To analysis the characteristics of oxidation, the sample is taken out of the petri dishes. After sample pretreatment, the sample contains no organic components and other impurities, only dry carbon. Put the sample into the platinum crucible and begin the thermogravimetric experiment. In the experiment, the oxidizing gas is pure oxygen (purity 99.99%), flow rate is 40 mL/min, and the protection gas is nitrogen (purity 99.999%), flow rate is also 40 mL/min. Simultaneously, the internal temperature is heated from 50 °C to 900 °C with 15 °C/min of heating rate in the experiment to obtain the thermogravimetric curve and then analyze the activation energy (Ea) and other parameters.

2.4. Parameter calculation

2.4.1. Aggregates fractal dimension (Df)

Soot particles have irregular and complex morphological structure. Fractal dimension is usually used to describe the degree of density among primary particles and the degree of geometric structure irregularity. This parameter is dimensionless. In general, the larger the fractal dimension, the more compact the structure of the aggregates, and the higher the overlap between the primary particles that make up the aggregates. The smaller the fractal dimension, the more “porous” the aggregates, and the lower the overlap between the primary particles:

\[
N_p = k_g \left( \frac{R_g}{r_p} \right)^{D_f}
\]

(1)

where \(k_g\) is the fractal prefactor, which is related to the radius of

![Fig. 7. Mean primary particle diameter of different fuels under different operation conditions.](image1)

![Fig. 8. Primary particles morphologies of different fuels with different loads.](image2)
rotation; \( r_p \) is the average radius of the primary particles. \( D_f \) calculate the obtained fractal dimension. \( N_p \) denotes the number of primary particles in the aggregates, which can be obtained according to the projection area of the aggregates through the following relation (2):

\[
N_p = k_a \left( \frac{A_a}{A_p} \right)
\]

(2)

\( A_a \) is the projected area of the aggregates, \( A_p \) is the projected area of the primary particles, and \( a \) and \( k_a \) are the empirical constants. According to the international common empirical data [39], here \( a \) is set to 1.19, and \( k_a \) is set to 1.81.

\( R_g \) can be found out through the following relation:

\[
L \pm 1.5 \, 0.05 \, \frac{R_g}{2R_g} = 1.5 \pm 0.05
\]

(3)

here, \( L \) is the maximum projection length of the aggregates.

Therefore, using image-pro Plus (Media Cybernetics) software to process and analyze TEM images, the parameters in the above formula (\( r_p, A_a, A_p, L \)) can be obtained to calculate the fractal dimension of particles under various working conditions.

Fig. 9. The La of primary particles of different fuels.
When the heating rate is constant, the kinetic equation of the reaction between particles and O2 can be expressed as:

\[
\frac{db}{dT} = \frac{1}{c} \cdot k(T) \times f(a)
\]  

(9)

b is the weight loss rate of carbon smoke at time T(T); C is a constant rate of temperature rise dT/dt; f(a) is a function related to the weight loss rate b; K(T) is the reaction velocity constant at time T(T) that satisfies the Arrhenius equation:

\[
\ln k(T) = \ln A - \frac{E_a}{RT}
\]  

(10)

\[f(a) = (1 - a)^n\]  

(11)

Substitute (10) and (11) into Eq. (9):

\[
\frac{D\log(1 - b)}{D\log(1 - b)} = -\frac{E_a}{2.303R} \times \frac{D(\log(1 - b))}{D(\log(1 - b))} + n
\]  

(12)

\[X = \frac{D(\log(1 - b))}{D(\log(1 - b))}\]  

(13)

\[Y = \frac{D(\log(1 - b))}{D(\log(1 - b))}\]  

(14)

\[a_0 = -\frac{E_a}{2.303R}\]  

(15)

The equation can be simplified to the following linear equation:

\[Y = a_0X + n\]  

(16)

A line with slope a0 and intercept n can be obtained by plotting X-Y with the graph method. The slope value a0 and intercept value n can be obtained by fitting the line, and then Ea can be calculated.

3. Results and discussion

3.1. Aggregate morphology distribution and nanostructure parameters of different fuels

The particulate morphology and its formation processes have been extensively investigated in the last few decades. PMs emitted from CI engines are widely observed as grape-like or chain-like aggregates composed of several tens to hundreds of nearly “spherical” particles [42]. Figs. 2 and 3 confirm the point by different fuels under different operation conditions. The agglomerates are polydispersed (various compactness) and comprise primary particles with sizes mostly between 20 and 30 nm, consistent with TEM observations by [43]. As seen from the Figs. 2 and 3, aggregates reduce with the addition of DMM, resulting in a decreased soot mass in the same condition, attributed to the absence of C-C bonds in structure and the replacement of C2H4 by C2H8O2 [12,13], hinder the increase of the five-membered rings and six-membered rings, leading to a decreased particles growth with the coagulation of PAH (polycyclic aromatic hydrocarbon) molecules. Therefore, the mass of soot reduces [30].

With the increased load, the mass of the aggregates increases considerably as shown in Fig. 2, regardless of the fuel used. It also conforms to the soot emissions in Fig. 4. The reason can be attributed to the increase in injection mass and decrease in air-fuel ratio (as shown in Table 4). Therefore, the insufficient oxygen hinders the combustion of oxidation process in the later combustion phase. Moreover, the higher mass of fuel promotes the increase of inception and precursors of soot. Therefore, the mass of aggregates increases with the increased loads. However, with the increase in speed, little change can be seen (Fig. 3).

To understand the structure of aggregates more fully, concretely, and quantitatively, the factors of aggregates fractal dimension (Df) is provided under the condition of 1400 and 2200 rpm with different
loads (0.6, 1.2 MPa). As can be seen from Fig. 5, the fractal dimension (Df) indicates the structural compactness of aggregates, and a lower fractal dimension value indicates less compact fractal morphology [29]. Fig. 5 shows the fractal dimension of different aggregates with different conditions. With respect to D100, diesel–DMM fuels have a lower Df irrespective of the operation condition. That means that soot from the DMM–diesel fuels is less compact than that from diesel. The reason is that the oxygen atom improves combustion environment, leading to a better soot oxidation. Besides, adequate oxygen content hinders the progress of soot’s growth, although the nuclear of soot has been formed. It is worthy knowing that the Df reduces with increased load under the same fuel conditions when the speed is 1400 rpm. However, when the speed is up to 2200 rpm, the Df increases with increased load. This may be due to the drop of residence time of soot when the speed increases from 1400 to 2200 rpm, resulting in less oxidation time in the cylinder, although the in-cylinder temperature increases with increased load. Further observations result in the conclusion that the use of DMM reduces the compactness of aggregates, possibly leading to easy oxidation of exhaust soot in the post treatment equipment [29,42].

### 3.2. Primary particulates and its nanostructure parameters

Fig. 6 shows the size distributions of soot primary particles of different fuels under different conditions. As seen from Fig. 6, the diameter distributions of all samples display a similar Gaussian distribution, with the range of sample diameters being from 10 to 45 nm. However, there
is a slight change in peak primary particle size. As the same level of operation conditions, the primary particles of blending fuels have smaller size distribution than that of diesel. For example, at the condition of 0.6 MPa and 1400 rpm, with the addition of DMM, the peak primary particle size ranges from 23–25 nm to 20–23 nm. For the same fuels, with an increase of load, the peak primary particle size also increases, especially compared with Fig. 6(j) to (l). Moreover, it is interesting to find that the size of blending fuels is more homogeneous than diesel, based on the large proportion of 15% above of certain diameter in the total amount about blending fuels, irrespective of the operating condition.

Fig. 7 displays the changes to mean primary particle diameter (dp) with different operation conditions. The dp of DMM–diesel fuels slightly decrease compared with that of D100. For the same condition of 1400 rpm and 0.6 MPa, both DMM6.4 and DMM13 are 1.129 nm (4.85%), and 2.078 nm (8.96%) smaller than D100 in the mean of dp, respectively. The smaller particles upon the addition of DMM to diesel suggests that most particles from aggregates have decreased diameter with respect of D100. This would be explained by the lower compactness of aggregates, attributing to sufficient oxygen concentration with DMM. Moreover, the smaller the primary particles, the larger the specific surface area is, attributing to the more active sites that provide oxygen attacked; therefore, it promotes the oxidation reactions in the exhaust and after-treatment system [44].

At the same fuel level, with the load and speed increased gradually, the mean particle diameters increase. For example, compared with the condition of 0.6 MPa and 1400 rpm of D100, the case of 1.2 MPa – 1400 rpm, 0.6 MPa – 2200 rpm, and 1.2 MPa – 2200 rpm increases by 1.164 nm (7%), 2.08 nm (8%), and 6.296 nm (27%), respectively, in terms of diameters. The reason is that the higher fuel-to-air ratio accelerates precursor growth and nucleation process at the high engine load; in addition, particulate oxidation is impeded simultaneously [45]. Besides, with the increase of speed, the residence time drops and the progress of oxidation decreases further. Therefore, the mean particle diameters increase, in line with previous reports [46,47].

Fig. 8 reveals the morphology of primary particulates of different fuels. The structure of “inner core-outer shell” can be seen for all samples, in line with previous literature [28]. In terms of the inner core, the fine particles have a nucleus approximately 5 nm at the central portion, and the nucleus is formed by several carbon layers, which exhibits a distorted structure [40]. These distorted structures contain both five-membered rings and six-membered rings, caused by particle growth with the coagulation of PAH (polycyclic aromatic hydrocarbon) molecules [30]. However, Ishiguro et al. [28] concluded that soot particles within the inner core have distinct round boundaries, partly consistent with that seen in Fig. 8. The shell comprises micro-crystallites with periodic orientation of graphic structure [16,18]. Gradually, due to condensation of small chemical species and surface reaction promoted by molecules, radicals, or ions including two to four carbon atoms, graphitic crystallites have been formed. The HRTEM images indicate little difference between D100 and DMM/diesel mixing fuels under different loads.

In this study, more than 150 primary particulates are selected from different aggregates. Three parameters fringe length (La), fringe separation distance (d), and fringe tortuosity (Tf) are used to describe the characters of soot nanostructures. Fig. 9 displays the change in fringe length of primary particles of different fuels. For all fuels and under all conditions, the distribution of La shows a single peak, and the distribution range is from 0.2 nm to 3.6 nm. As can be seen from the distribution diagram, La is more affected by the load and less affected by the fuel and rotation speed. With the increase in load, the distribution diagram of La shows an increase, indicating that the proportion of longer chains of microcrystals increases.

The mean fringe length is shown in Fig. 10. It is concluded that La generally increases with increased load and speed for the same fuel level between 1.1 nm and 1.7 nm. For instance, with respect to the case of 0.6 MPa–1400 rpm, the case of 1.2 MPa–1400 rpm, 0.6 MPa–2200 rpm, and 1.2 MPa–2200 rpm of D100, there was an increase in La by 0.22 nm (18.9%), 0.09 nm (7.8%), and 0.3 nm (25.7%), respectively. Under the same operating conditions such as 0.6 MPa–1400 rpm, both the fuel of DMM6.4 and DMM13 increased by 0.067 nm (5.7%) and 0.071 nm (6.1%), respectively. The results show that with an increase in load and speed, the basic structure of microcrystalline carbon particles change, because carbon particles within the short-chain part than the surrounding carbon layer part are easier to burn, the short-chain part gradually disappears, and the proportion of the long chain gradually increases, resulting in a gradual increase in the crystallite La; therefore, the structure of the carbon particles is more layered and stable.

Fig. 11 displays the change in fringe separation distance of primary particles of different fuels. For all fuels and under all conditions, the distribution of d shows a single peak, and the distribution range is from 0.28 nm to 0.44 nm. As seen from the distribution diagram, d is affected by the fuel, load, and speed. With the use of DMM–diesel blends, the distribution range of fringe separation distance becomes increasingly larger, and the average fringe separation distance of primary particles tends to increase. With the increase of load and speed, the distribution range of fringe separation distance narrows, and the average fringe separation distance of primary particles tends to decrease.

We can see that with increased loads and speed, the primary particles gradually change to graphitization in Fig. 12, but at a larger distance than the layers of graphite crystals because the primary particles contain other atomic components besides carbon; these atoms enter the layers of graphite crystals, thereby increasing the distance between the layers [29,30]. With the gradual reaction of other atoms in the middle of the shell's multi-layer microcrystalline carbon layer, the torsion and translation between the carbon layers gradually reduce the layer separation distance, and finally reach the average layer spacing, which is still higher than 0.3376 nm of graphite.

Fig. 13 displays the change in fringe tortuosity of primary particles of different fuels. For all fuels and under all conditions, the distribution of Tf shows a single peak, and the distribution range is from 1.0 nm to 1.8 nm. As can be seen from the distribution diagram, Tf is considerably more affected by the load than the fuel and speed. With the increase in load, the distribution range of fringe tortuosity decreases, and the average fringe tortuosity of primary particles tends to decrease.

A larger fringe separation could facilitate an oxygen reaction with edge-site positions. Besides, lamella tortuosity induces ring strain into the carbon structure to expose more individual atoms [16]. Moreover, the atomic structure of carbon layer also shows that the larger curvature of carbon layer is not stable, more easily by oxidation, so smaller curvature carbon layer take a greater proportion gradually, thus lead to the combustion process with high load, the curvature of the carbon layer is reduced gradually to stable, as seen from Fig. 14.
3.3. Oxidation reaction of different fuels with different operating conditions

Fig. 15 shows the thermogravimetric (mass loss) curves with different fuels and different conditions. Both fuels as well as operating conditions can change the oxidation reactions of soot particles. As seen from the Fig. 15, fuel D100 can be easily oxidized under the four operating conditions, compared with DMM6.4 and DMM13. In addition, the higher the proportion of DMM, the more difficult oxidation is, indicating higher graphitization degree of soot in the exhaust gas. Moreover, as the load increase, the start temperature of oxidation rises with the same speed as shown in Fig. 15(a) and (b).

To better understand the oxidation reaction of soot with different fuels and conditions, apparent reactive energy (Ea) is accepted to quantificationally describe the difference between D100, DMM6.4, and DMM13 as shown in Fig. 16. In this study, the range of Ea is between 143 kJ/mol and 155 kJ/mol, which is lower than 200 kJ/mol, indicating the formed amorphous framework in the soot particulates. As soot with an unformed framework would tend to be oxidization better, a lower Ea is needed. With the addition of DMM, the Ea increases, suggesting a more regular and higher degree of graphitization than D100 within soot particles. This could be that on the one hand, the oxygen content within fuels promotes oxidation progress in diffusion phase; on the other hand, the higher exhaust temperature provides sufficient oxidation energy (as shown in Table 4). Therefore, more regular and higher degree of graphitization are formed. As the load and speed increase, a higher fuel-to-air ratio and shorter residence time...
hinder the oxidation progress, leading to a large amount of unformed soot particulate.

3.4. Relationship between nanostructure and oxidation of different fuels

Fig. 17 shows the relation between nanostructure parameters and apparent reactive energy of different fuels. It is observed that there exists a significant association between nanostructure parameters and apparent reactive energy. As shown in Fig. 17(a) and (c), soot with smaller primary particulate diameter and the distance between adjacent layer planes (d) demonstrates higher $E_a$, consistent with Wang et al.’s findings [43]. In addition, soot with higher length of graphene layer (La) and the ratio of the actual fringe length to the straight-line distance exhibits higher $E_a$, in line with previous studies [36,48]. The nanos- tructure influences the oxidation reaction of graphene segments, thereby, leading to a difference in soot oxidation.

4. Conclusion

A comprehensive investigation of the morphology of particulates
fueled with neat diesel and oxygenated fuels DMM (DMM6.4 and DMM13) has been conducted. The following conclusions are drawn.

1. Addition of DMM to diesel produces smaller primary particulates. In this investigation, DMM13 displays the smallest primary particulates, followed by DMM6.4 and D100. The fuels plays a predominant role in the inception and precursor of soot formation and after-treatment equipment.

2. Diesel–DMM fuels have a lower Df irrespective of the operating condition. This means that soot from the DMM–diesel fuels is less compact than that from diesel, and the “inner core-outer shell” structure can be seen for all samples.

3. Operating conditions have a considerable influence on the fuel nanostructure. With an increase in the load and speed, the distance of the graphene layers (La) increases and the distance between adjacent layer planes (d) decreases.

4. With the addition of DMM, a more regular and higher degree of graphitization than D100 within soot particles is observed. The nanostructure influences the oxidation reaction of graphene segments, leading to a difference in soot oxidation.

We herein observed that the use of DMM–diesel fuels can reduce the formation of primary particles of exhaust soot. Simultaneously, the particle size of the primary particles decreases, the lattice length of the particles increases, the layer spacing decreases, and the oxidation activation energy increases. Therefore, post-treatment equipment for DMM–diesel fuel particles should improve their oxidation capacity, especially under low loads and low speeds. In the case of high loads and high speeds, the oxidation capacity of post-treatment equipment decreases, however, the processing efficiency and maximum bearing capacity of the post-treatment equipment increase. This study has certain reference value for the treatment of DMM particles, and essentially achieves the goal of this experiment.

**Author contributions**

MZP (Mingzhang Pan) and JUW (Jiangjun Wei) conceived and designed the analysis. WWQ (Weiwei Qian) and HZH (Haozhong Huang) wrote the paper and collected the data. RH (Rong Huang) and JL contributed data and analysis tools and performed the analysis. MZP, JUW, WWQ, HZH, RH and JL reviewed and edited the manuscript. All authors read and approved the manuscript.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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