Full Length Article

An investigation on the characteristics of and influence factors for NO\textsubscript{2} formation in diesel/methanol dual fuel engine

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ABSTRACT

It had been found in previous experimental studies that the compression ignition engine with Diesel/Methanol Compound Combustion (DMCC) could significantly increase nitrogen dioxide (NO\textsubscript{2}) emission, compared with conventional diesel mode. However, the detailed formation process and influence factors of NO\textsubscript{2} in Diesel/ Methanol Dual Fuel (DMDF) engine have not been reported previously. In order to investigate the mechanism of increased NO\textsubscript{2} and effect factors of NO\textsubscript{2} emission, following works were conducted: Firstly, in light of the literature researches, a hypothesis concerning the NO\textsubscript{2} formation procession in DMDF engine was presented, whose demonstration was realized by using numerical simulation; Secondly, the experiments about the effect of methanol substitute proportion (MSP), exhaust gas recirculation (EGR) and exhaust backpressure on the NO\textsubscript{2} emission were conducted, whose results were analyzed by using the proved hypothesis. The results of simulation justified that compared with diesel case, the existence of methanol premixed region in DMDF mode was the main cause of increased NO\textsubscript{2}, and the impact of temperature on the NO\textsubscript{2} emission mainly lay in that of temperature on hydroperoxyl (HO\textsubscript{2}) radicals. The experiments showed that along with the increase of MSP, NO\textsubscript{2} emission increased firstly and then decreases. The addition of EGR could lead to the reduction of NO\textsubscript{2}, while the slight increase of exhaust backpressure would increase total nitrogen oxides (NO\textsubscript{x}) emission.

Keywords:
Diesel/methanol dual fuel
NO\textsubscript{2} emission
Hydroperoxyl (HO\textsubscript{2}) radicals
Influence factors

1. Introduction

Due to the high thermal efficiency and fuel economy, diesel engines have been widely exploited in many fields [1]. However, as the problem of environmental pollution getting severer, every country begins to establish more rigorous emission regulations, which put forward higher requirements for diesel engine development. Clean alternative fuel, as effective ways, has been widely investigated in recent years, including natural gas, hydrogen, methanol, ethanol and so on [2–6]. DMCC is one of the effective ways, where methanol is injected into the intake manifold, and diesel is directly injected into the cylinder. Because of the difference from emulsification approach, where methanol is blended with diesel before injection, DMCC is also called fumigation approach. According to the previous researches, DMCC can realize the reduction of NO\textsubscript{x} and soot emissions simultaneously [4,7–9].

However, previous experimental studies had found that compared with conventional diesel mode, the compression ignition engine with DMCC could significantly increase nitrogen dioxide (NO\textsubscript{2}) emission [1,7,10]. In the meantime, many other researches had also discovered that the addition of methanol or other oxygenated fuel could dramatically augment the NO\textsubscript{2} emission, which led to the higher NO\textsubscript{2}/NO rate than diesel mode. For example, Cheng et al. [11] found that different ways of adding methanol to biodiesel had disparate effects on NO\textsubscript{2} emission. Methanol fumigation increased the NO\textsubscript{2} emission considerably, while the NO\textsubscript{2} emission in methanol emulsified mode was same as that in the biodiesel case. They asserted that the increase of NO\textsubscript{2} lay in the hydroperoxyl (HO\textsubscript{2}) free radicals produced by methanol. Cheung et al. [12] investigated experimentally the impact of adding ethanol to ultralow-sulfur diesel (ULSD) on the regulated and unregulated emissions. They discovered that as the addition of ethanol in ULSD, NO\textsubscript{2} emission increased gradually, where they held the viewpoint that the cooling effect of ethanol was responsible for the increase of NO\textsubscript{2}. Wei et al. [13] explored the influence of n-pentanol addition on the combustion and emission characteristics in a diesel engine. Similarly, they found that with the increase of n-pentanol, the NO\textsubscript{2} emission

Abbreviations: DMCC, diesel/methanol compound combustion; NO\textsubscript{2}, nitrogen dioxide; DMDF, diesel methanol dual fuel; MSP, methanol substitution proportion; HO\textsubscript{2}, hydroperoxyl; NO\textsubscript{x}, nitrogen oxides; NO, nitrogen monoxide; ECU, electronic control unit; CA, crank angle; HRR, heat release rate; ATDC, after top dead center; TDC, top dead center; CA05, the 5% mass fraction burned combustion timing

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exhibited an increasing trend at each engine load, where they explained that the decreased in-cylinder temperature and HO2 free radical both contributed to the increase of NO2.

Although being a kind of the gas pollutant for our environment, NO2 has great research value in after-treatment system. For instance, NO2 plays an important role in the passive regeneration of diesel particulate filter (DPF) [14], due to its strong oxidation characteristics. And the NO2/NO ratio can effectively influence the SCR system efficiency [15]. Hence, as the development of researches concerning DMCC or other oxygenated fuel, the investigation of formation characteristics and influence factors of NO2 emission in fumigation approach of oxygenated fuel will be crucial. However, previous researches merely point out the possible relations of HO2 radicals and temperature to the NO2 formation without elaborating on the formation process and effect details when adding oxygenated fuel to diesel engine. In this paper, a hypothesis of NO2 formation in DMDF engine was presented and validated with simulation approach. Besides, in order to explore the influence factors of NO2 emission in the same engine, the effects of MSR, EGR and exhaust backpressure on the NO2 emission were investigated with experiment.

2. Characteristics of NO2 formation in DMDF engine

2.1. NO2 mechanism

NO2 mechanism mainly contains NO2 formation mechanism and dissociation mechanism, which have been widely investigated [16–20]. The formation mechanism widely accepted is when touched by HO2 radicals, the NO formed in the flame zone can be rapidly converted to NO2 via the reaction: NO + HO2 + O → NO2 + OH [16,17], and the formation of NO2 is mainly affected by the mixture temperature and concentration of NO and HO2. It should be noticed that when the combustion temperature reaches the threshold value, which is usually 1200 K, the HO2 radicals cannot make stable existence. Because in high temperature condition, it is difficult for the oxygen to generate stable peroxide by combining with fuel molecule, and the consumption of HO2 will increase rapidly [21].

On the other hand, the NO2 can also be converted to NO via the reaction: NO2 + O → NO + O2, and NO2 + H → NO + OH [17,22]. An widely accepted outlook concerning NO2 destruction is when the NO2 is mixed with cooler fluid, which could be the cool mixture that is far from the burning region, dissociation reaction can be quenched, which will lead to the high NO2/NO ratio [17].

2.2. Computational model

To uncover the characteristics of NO2 formation in DMDF engine and verify the relevant hypothesis, the numerical simulation approach is utilized. This simulation use commercial CFD software CONVERGE as the computation platform. The Kelvin–Helmholtz (KH)-Rayleigh Taylor (KH-RT) model [23] was employed to model the droplet breakup process, and the O'Rourke model [24] was applied for the collision simulation of diesel spray droplets. In addition, to balance the computation time and accuracy, this paper chose a reduced n-heptane/methanol mechanism [25], containing 44 species and 65 reactions, as the DMDF combustion mechanism, which added a NOX and a soot mechanism to the skeletal mechanism from Xu et al. [21] and had been proved to be suitable for the in-cylinder simulation for both pure diesel and DMDF mode. The NOX mechanism in this paper was added from GR1D3.0 [26], which mainly contained 7 reactions. Besides, the renormalization group (RNG) k-ε model was used as the turbulence model, referring to the suggestion of Zang et al. [25]. And the wall heat transfer was modeled according to Angelberger [27]. The SAGE detailed chemistry solver [28] was adopted to simulate the combustion process and solve the reaction rates, where a turbulence timescale is not used to slow down the combustion rate. SAGE calculates the reaction rates for each elementary reaction while the CFD solver solves the transport equations. The calculation process of reaction rates in SAGE solver is briefly explained as follows [28].

A multi-step chemical reaction mechanism can be written in the form [29]:

\[
\sum_{j=1}^{I} \nu_j \chi_j \leftrightarrow \sum_{j=1}^{I} \nu'_j \chi'_j \quad \text{for } i = 1, 2, \ldots, I
\]

(1)

where \( \nu_j \) and \( \nu'_j \) are the stoichiometric coefficients for the reactants and products, respectively, for species \( j \) and reaction \( i \), and \( \chi_j \) represents the chemical symbol for species \( j \). The net production rate of species \( j \) is given by:

\[
\dot{n}_j = \sum_{i=1}^{J} \nu_j q_i \quad \text{for } j = 1, 2, \ldots, J
\]

(2)

where

\[
\nu_j = \nu'_j - \nu''_j
\]

(3)

and the rate-of-progress variable \( q_i \) for the \( i \)th reaction is calculated from the Eq. (4)

\[
q_i = k_i \prod_{j=1}^{I} [X_j]^{\nu_j} - k_{-i} \prod_{j=1}^{I} [X_j]^{\nu'_j}
\]

(4)

where \([X_j]\) is the molar concentration of species \( j \), and \( k_i \) and \( k_{-i} \) are the forward and reverse rate coefficients for reaction \( i \). In SAGE, the forward rate coefficient is expressed by the Arrhenius formula, and the reverse rate coefficient can either be specified by the Arrhenius formula, or calculated from the equilibrium coefficient \( K_{eqi} \):

\[
k_i = \frac{k_{fi}}{K_{eqi}}
\]

(5)

Technical specifications of the experimental engine are listed in Table 1. Because the diesel injector has seven nozzle holes, a 51.4° mesh was used in this study, and the computational mesh is shown in Fig. 1.

Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cylinders</td>
<td>Four in-line</td>
</tr>
<tr>
<td>Displacement</td>
<td>4.214 L</td>
</tr>
<tr>
<td>Bore × stroke</td>
<td>108 × 115 mm</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>17:1</td>
</tr>
<tr>
<td>Maximum power</td>
<td>1031 kW/1600 r/min</td>
</tr>
<tr>
<td>Piston geometry</td>
<td>ω type</td>
</tr>
<tr>
<td>Inlet valve closing</td>
<td>– 130.3 °CA ATDC</td>
</tr>
<tr>
<td>Exhaust valve opening</td>
<td>112.2 °CA ATDC</td>
</tr>
<tr>
<td>Injection pressure</td>
<td>28 MPa</td>
</tr>
<tr>
<td>Nozzle (number × bore diameter)</td>
<td>7 × 0.16 mm</td>
</tr>
</tbody>
</table>

Fig. 1. Computational mesh of engine simulations.

2.3. Hypothesis of NO2 formation in DMDF engine and its demonstration

2.3.1. Hypothesis of NO2 formation in DMDF engine

According to the previous researches, there are obviously differences in NO2 emission between different approaches of adding methanol in DMDF mode [11]. In emulsification mode, the methanol, which is emulsified with diesel outside cylinder, is directly injected into the cylinder, and burned as a diffusion flame. Nevertheless, in DMCC or...
Fumigation mode, diesel is directly injected into the cylinder, while methanol is injected into the intake manifold, which leads to three different regions in the cylinder, shown as Fig. 2. Mixture zone of diesel and methanol will be ignited first, resulted from the suitable equivalence ratio. High concentration zone of diesel will be burned in diffusion combustion, just like conventional diesel engine, which can provide the energy for the flame propagation of methanol premixed region.

In this paper, through comparing the combustion patterns between emulsification and fumigation mode, the existence of methanol premixed region, shown as Fig. 2, is regarded as the main reason for increased NO2 emission, because the reactions there can produce HO2 radicals and the broad range of temperature is beneficial to the conservation of HO2. As mentioned above, HO2 is very sensitive to high temperature. High temperature will do harm to HO2 formation and accelerate its consumption, so the proper middle temperature zone can provide sufficient time for NO to combine with HO2, and then to produce NO2.

In addition, through comprehensively considering the effect of methanol fumigation on the formation and destruction reactions of NO2 in DMDF engine, the ultimate NO2 emission is thought to be mainly affected by the formation process of NO2, i.e. the formation of NO2, is regarded as the main reason for the influence of temperature on NO2 emission, although temperature can also affect the destruction of NO2.

2.3.2. Demonstration of the hypothesis

To justify the hypothesis, the approach of numerical computation approach was employed. Before the demonstration of hypothesis, the simulation results were validated with experimental data of DMDF engine at two operation cases. One is the MSP30 mode, which was conducted at 1660 r/min, 220 N·m torque. Based on the mass consumption rates of diesel and methanol, the MSP can be calculated by using Eq. (6)

$$\text{MSP} = \frac{q_{m,\text{dd}} - q_{m,\text{dm}}}{q_{m,\text{dd}}} \times 100\%$$

where $q_{m,\text{dd}}$ is diesel fuel consumption rate (kg/h) in neat diesel mode; $q_{m,\text{dm}}$ is diesel fuel consumption rate (kg/h) in DMDF mode.
And the other is diesel mode, which is operated at the same operation condition without methanol. The comparisons of cylinder pressure and HRR between calculations and measurements at two operation cases are shown in Fig. 3. The pressure and HRR of simulations agree with the experimental data well. According to Zang et al. [25], the clear difference in HRR between simulation and experiment in MSP30 mode, shown as Fig. 3(b), is because of the inappropriate definition of the heat capacity ratio in the derivation of HRR in a combustion analysis system (AVL Indicom) in experiments. The HRR in experiment is calculated in light of the cylinder pressure by Eq. (7)

$$\frac{dQ_g}{dp} = \frac{\gamma V dp}{\gamma - 1} - \frac{1}{\gamma - 1} P \frac{dV}{dp} + \frac{dQ_w}{dp}$$

where \( \frac{dQ_g}{dp} \) is HRR, \( \gamma \) is the heat capacity ratio, \( V \) is the instantaneous volume, \( P \) is cylinder pressure, and \( dQ_w/dp \) is heat loss rate. \( \gamma \) of mixture gas is influenced by the species and temperature in cylinder. Generally, the empirical value of \( \gamma \) is suitable for experimental HRR calculation in diesel mode, which can be seen in Fig. 3(a). Whereas, the appropriate \( \gamma \) for DMDF mode has not been settled, which leads to the overestimation.

Fig. 4 shows the comparison of \( \text{HO}_2 \) between two modes. Compared with diesel mode, \( \text{HO}_2 \) mole fraction in MSP30 case is much higher, and its conservation duration is much longer, which justifies that the addition of methanol can considerably boost the formation and conservation duration of \( \text{HO}_2 \). Fig. 5 exhibits the variation trend of in-cylinder temperature, \( \text{NO}, \text{HO}_2 \) and \( \text{NO}_2 \) in MSP30 case and the legends above the cloud charts show the value of Kelvin temperature, and the mole fraction of species. In DMDF mode, diesel, directly injected, is ignited by compressing firstly and then functions as the ignition source to the peripheral premixed methanol, shown as the Fig. 5(a) at 10 ATDC. As the development of combustion, the formation region of \( \text{NO} \) is in line with the high temperature area, which is higher than 2000 K, while the region of high \( \text{HO}_2 \) concentration is located in the relatively middle temperature zone, which conforms to the sensitivity of \( \text{HO}_2 \) to high temperature. Moreover, nearly all of \( \text{HO}_2 \) are generated in the methanol premixed region. The generation of \( \text{NO}_2 \) begins in the overlap zone between formation region of \( \text{NO} \) and \( \text{HO}_2 \), and the region of high \( \text{NO}_2 \) concentration corresponds with that of \( \text{HO}_2 \) strictly, which demonstrates that the existence of methanol premixed region is essential to the generation of \( \text{NO}_2 \), and thus it is the main reason for the increased \( \text{NO}_2 \) emission in DMDF mode.

Fig. 6 shows the variation trend of in-cylinder temperature, \( \text{NO}, \text{HO}_2 \) and \( \text{NO}_2 \) in MSP30 case.
HO2 and NO2 in diesel case, which use the same scale of legends as the MSP30 case. In diesel mode, the premixed small amount of diesel is ignited firstly by compression, and then the diffusion flame comes into being, as shown in Fig. 6(a). The formation region of NO is in accord with high temperature zone, and the generation zone of HO2 is situated in the middle temperature zone, just like the MSP30 case. However, in contrast to MSP30 case, HO2 radicals generated from middle temperature region of the spray in diesel case begin to dive from 0 ATDC to 10 ATDC, shown as in Fig. 6(c) and Fig. 4, because the high temperature oxidation process of the fuel is dominant in the diffusion combustion [30] and the duration of middle temperature zone is very short, which result in the considerable decrease of the contact time between NO and HO2 and the consequent restraint of NO2 formation. The formation of NO2 still starts from the overlap zone between formation region of NO and HO2, shown as Fig. 6(d), but without sufficient premixed zone, which is beneficial to the generation and conservation of HO2, the amount of NO2 generated in the diesel mode is so limited, when compared with MSP30 case.

Fig. 6 exhibits the variation trend of NO and NO2 in MSP30 case. As the figure shown, mole fraction of NO soars from 0 to 20 ATDC and then decreases gradually, which is due to the transformation to NO2, while the mole fraction of NO2 increase gradually. Provided that the destruction reaction of NO2 plays an important role in the NO2 emission, the amount of NO2 will show the trend of decrease in the late period of reaction (after 60 ATDC), because the generation of NO2 is limited by the amount of HO2, rather than keep increasing. So the continuous increment of NO2 indicates that in DMDF mode, the effect of NO2 destruction is negligible for the NO2 emission, and the mole fraction of NO2 will maintain increasing, as long as the HO2 radicals exist. Therefore, the ultimate NO2 emission is mainly determined by the formation reaction of NO2, and due to the previous results that temperature can influence the NO2 emission [7,17], it is reasonable to say that the effect of temperature on NO2 emission mainly lies in that of temperature on conservation of HO2.
3. Experimental apparatus and method

3.1. Experiment setup and fuels

Fig. 8 shows the schematic of the engine layout. The original engine was an in-line four-cylinder, direct injection, turbocharged diesel engine with an electronically controlled unit injection pump. Technical specifications of the engine are listed in Table 1. In order to operate DMDF mode, the engine was modified with a methanol rail and four methanol injectors, which were added to the intake manifold. The methanol was injected under the pressure of 0.5 MPa to form homogeneous methanol/air mixture and the mass of methanol injected was controlled by an electronic control unit (ECU) developed by ourselves. Injection timing and quantity of diesel were controlled by the ECU of the original diesel engine, and the methanol injection system was wholly independent of the diesel ECU. The engine was coupled to an electronically controlled hydraulic dynamometer. Engine speed and torque could be controlled by the EMC2020 engine test system. Diesel and methanol fuel consumptions were independently measured gravimetrically using two coriolis meters with the precision of 0.1 g. Intake temperature was controlled by the coordination of an intercooler and coordinate of an intercooler and EGR cooler.

![Diagram of experimental setup](image)

**Fig. 8. Schematic of experimental setup.**

<p>| Table 2 |
| Properties of two fuels. |</p>
<table>
<thead>
<tr>
<th>Properties</th>
<th>Diesel</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20 °C (kg/m³)</td>
<td>819.8</td>
<td>790</td>
</tr>
<tr>
<td>Low heating values (MJ/kg)</td>
<td>42.5</td>
<td>19.7</td>
</tr>
<tr>
<td>Content of C (%)</td>
<td>86</td>
<td>38</td>
</tr>
<tr>
<td>Content of H (%)</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Content of O (%)</td>
<td>–</td>
<td>50</td>
</tr>
<tr>
<td>Sulfur (mg/kg)</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Autoignition temperature (°C)</td>
<td>≈250</td>
<td>450</td>
</tr>
<tr>
<td>Latent heat of evaporation (kJ/kg)</td>
<td>250</td>
<td>1110</td>
</tr>
<tr>
<td>Cetane number</td>
<td>54.7</td>
<td>3–5</td>
</tr>
<tr>
<td>Burning range (%)</td>
<td>1.4–7.6</td>
<td>5.5–26</td>
</tr>
<tr>
<td>Kinematic viscosity at 20 °C (mm²/s)</td>
<td>3.564</td>
<td>–</td>
</tr>
</tbody>
</table>

**Fig. 7.** Variation trend of NO and NO₂ in MSP30 case.

**Table 3**

<table>
<thead>
<tr>
<th>Components</th>
<th>Experiment Case</th>
<th>Range</th>
<th>Accuracy (of full scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Effect of MSP</td>
<td>0–1000 ppm</td>
<td>±3.0%</td>
</tr>
<tr>
<td>NO</td>
<td>Effect of EGR</td>
<td>0–100 ppm</td>
<td>±3.0%</td>
</tr>
<tr>
<td>NO</td>
<td>Effect of backpressure</td>
<td>0–500 ppm</td>
<td>±3.0%</td>
</tr>
<tr>
<td>NO₂</td>
<td>Effect of MSP</td>
<td>0–500 ppm</td>
<td>±3.0%</td>
</tr>
<tr>
<td>NO₂</td>
<td>Effect of EGR</td>
<td>0–500 ppm</td>
<td>±3.0%</td>
</tr>
<tr>
<td>NO₂</td>
<td>Effect of backpressure</td>
<td>0–500 ppm</td>
<td>±3.0%</td>
</tr>
</tbody>
</table>

Injection timing and quantity of diesel were controlled by the ECU of the original diesel engine, and the methanol injection system was wholly independent of the diesel ECU. The engine was coupled to an electronically controlled hydraulic dynamometer. Engine speed and torque could be controlled by the EMC2020 engine test system. Diesel and methanol fuel consumptions were independently measured gravimetrically using two coriolis meters with the precision of 0.1 g. Intake temperature was controlled by the coordination of an intercooler and coordinate of an intercooler and EGR cooler.
an electric heater, with the precision of 2 °C. Diesel and methanol temperature was fixed at 25 °C, and controlled by the PID Temperature Controller. Engine coolant temperature and inlet air temperature were recorded by resistance thermometer sensors, while exhaust temperature was recorded using K type thermocouples with the accuracy of 0.1 °C. The diesel used in the test was commercial 0# diesel, of which sulfur content is less 10 ppm, while the methanol used was industrial grade with the purity of 99.99%. Table 2 shows the general properties of the two fuels. The amount of EGR is regulated by adjusting the EGR valve opening position and the exhaust backpressure, which is regulated by an exhaust backpressure valve downstream the exhaust pipe, and a shell and tube exchanger was used to reduce EGR temperature by fresh water. In this work, the EGR ratio is defined as the ratio of CO₂ concentrations in the intake and exhaust gases, shown as Eq. (8), and detected by Horiba MEXA-7100DEGR.

\[
\text{EGR ratio} = \frac{(\text{CO}_2)_\text{intake}}{(\text{CO}_2)_\text{exhaust}} \times 100\%
\]  

(8)

The NOₓ emissions were measured in exhaust systems by using Horiba MEXA-6000FT. Due to the negligible amount of N₂O, which is always less than 3 ppm in different conditions, the NOₓ emissions here merely consist of NO and NO₂. The measure range and accuracy are listed in the Table 3. The pressure trace in-cylinder was measured with a Kistler 6125CU20 piezoelectric pressure transducer in series with an AVL 612 IndiSmart combustion analyzer, which had a signal amplifier for piezo inputs. A shaft encoder with 720 pulses per revolution was used to send engine speed, which supplied a resolution of 0.5° crank angle (CA). For each engine operating point, 500 consecutive cycles of cylinder pressure data were recorded. The collected cycles were ensemble averaged to yield a representative cylinder pressure trace, which was used to calculate the heat release rate (HRR) by the AVL 612 IndiSmart combustion analyzer.

3.2. Engine operating method and test conditions

Experiments were conducted at different MSP, EGR ratios and backpressure, which changes the internal residual gas amount, and the engine speed was 1660 r/min with the output torque of 220 and 110 N·m, corresponding to engine loads of 50% and 25%. Throughout the whole test, the air temperature after intercooler was controlled at 35 ± 1 °C, while the cooling water temperature was fixed at 85 ± 1 °C. To investigate the combustion characteristics and NOₓ emissions under different experiment conditions, each experiment was carried out with the fixed diesel injection timing of −4°CA after top dead center (ATDC). In the experiment, firstly, to investigate the effects of MSP on combustion and NOₓ emissions, the engine operation condition was fixed, EGR valve was fully closed, and the MSP was controlled by regulating the mass of methanol injection. Then, to investigate the effect of EGR on combustion and NOₓ emissions in DMDF mode, the MSP was fixed at 30%, and the EGR valve was controlled to achieve the aiming EGR ratio. Although the exhaust backpressure here was not regulated to adjust EGR ratio, it is a common way for increasing EGR ratio by elevating the exhaust backpressure, so the effect of backpressure on combustion and NOₓ emissions were also investigated, where the MSP was fixed at 30%, EGR valve was fully closed, and the exhaust backpressure valve was controlled to reach the specific backpressure. The specific operation parameters are listed in the Table 4. At each test point, the period of operation was maintained for about 3 min, and experimental data was the weighted average of the data stream.

4. Experimental results and discussion

4.1. The effect of MSP on combustion

Fig. 9 illustrates the combustion pressure curves and the HRR curves for different MSP at 220 N·m torque. As Fig. 9 shows, with the increase of MSP, the ignition delay was prolonged, which effectively increased the premixed combustion ratio, due to the high vaporization latent heat and radicals conversion function of methanol. The increased heat release rate of premixed combustion could elevate the cylinder temperature of that crank angle, which would be beneficial to the later diffusion combustion of diesel and flame propagation combustion of methanol, and thus enhanced the cylinder pressure and temperature. However, it should be noticed that when the MSP were excessively high, like MSP50 and MSP60, the post period of combustion of diesel
and methanol deteriorated, because of the too little mass of diesel, which could largely decrease the cylinder pressure and temperature.

4.2. The effect of EGR on combustion

Fig. 10 illustrates the combustion characteristics for different EGR rates at MSP30, 110 N·m torque. Shown in the Fig. 10(a), along with the increase of EGR rate, the ignition delay was protracted, and the CA05 was retarded, shown as Fig. 10(b), due to the thermodynamic and chemical function of EGR and reduction of oxygen concentration [31]. The more time for premixing lead to the higher rate of premixing combustion, which is benefical to enhance the cylinder pressure and accelerate the post combustion of diesel and methanol, and thus shorten the combustion duration, as shown in Fig. 10(b).

4.3. The effect of exhaust backpressure on combustion

Fig. 11 shows the combustion characteristics of different exhaust backpressure in DMDF engine.

Fig. 12 illustrates the NOx emission characteristics for different MSP at 220 N·m torque. As shown in Fig. 12(a), with the increment of MSP, total NOx and NO emissions were decreased gradually, while the emission of NO2 was increased firstly and then decreased. In the meantime, the ratio of NO2 to NO, shown as Fig. 12(b), was found to keep increasing, along with the increase of MSP.

Due to the high vaporization latent heat of methanol, the increasing MSP can effectively lower the combustion temperature and reduce the local high temperature region [4], which will restrain the formation of NO. The change of NO2 emission can be explained by combining the
From MSP0 to MSP40, the equivalent ratio of methanol in the methanol premixed region increased gradually, which was beneficial to the increase of HO2 and facilitated the formation of NO2. However, the increase rate of NO2 was constrained, because of the reduction of NO emission and increase of heat release rate, which would do harm to the conservation of HO2. From MSP40 to MSP60, absolute value of NO2 emission began to reduce, since the deterioration of methanol post combustion led to the further reduction of NO, which can be confirmed by the continuous increase of NO2/NO, shown as Fig. 12(b).

4.5. The effect of EGR on NO2

Fig. 13 illustrates the NOX emission characteristics for different EGR ratios at MSP30, 110 N·m torque. As the elevation of EGR ratio, total NOX and NO2 emissions decreased gradually, while the NO emission decreased firstly and then keep almost constant. It should be noticed that the formation of NOX is a chain reaction. So, in fact, the reduction of total NOX was caused by the reduction of NO. Since EGR can reduce the oxygen content of intake air, and increase the heat capacity of mixture, it can effectively suppress the formation of NO [32], and then decrease the total NOX emission. Because of the reduction of NO formation and the shortening of combustion duration, which could be harmful to the conservation of HO2, the NO2 emission was decreased. On the other hand, the reduction of HO2, which could repress the conversion from NO to NO2, could be beneficial to the conservation of NO. Thus, the NO emission remain almost unchanged from EGR10 to EGR30.

4.6. The effect of exhaust backpressure on NO2

Fig. 14 demonstrates the NOX emission characteristics for different exhaust backpressure at MSP30, 110 N·m torque, without EGR. Shown in the Fig. 14, along with the increment of backpressure, all the NOX emissions, including total NOX, NO and NO2, are enhanced, while the increase rate of NO2 emission lowered gradually. Because of the high heat release rate and high combustion temperature consequently, the NO emission was increased, which was beneficial to the increase of NO2 emission. However, the conservation of HO2 was constrained by the high combustion temperature and the shortened combustion duration, leading to the reduction of NO2 increase rate. In the meantime, we can speculate logically that as the further elevation of backpressure, the
NO2 will begin to reduce, due to the further reduction of HO2.

5. Conclusion

In this paper, the hypothesis of formation characteristics of NO2 in DMDF engine was put forward and vindicated with numerical approach, and the impact of MSR, EGR and exhaust backpressure on NO2 emission were investigated utilizing 4-cylinder unit-pump diesel engine fueled with DMDF mode. The main conclusions are summarized as follows:

1) The addition of methanol in DMDF mode significantly increase the HO2 radicals and owing to the reactions producing HO2 and appropriate temperature range, the existence of methanol premixed region is the main reason for the increased NO2 emission. Moreover, the outlook concerning the NO2 formation characteristics in this paper can also apply to other oxygenated fuels case with fumigation approach.

2) In DMDF engine, the influence of temperature on the ultimate NO2 emission mainly lies in the impact of temperature on the NO and HO2 radicals, i.e. on the formation of NO2, rather than on the NO2 destruction. Thus, adjusting the formation and conservation of NO and HO2 radicals in the cylinder through regulating combustion temperature enables the control of NO2 emission.

3) As the continuous increase of MSP, NO2 emission increases firstly and then decrease gradually.

4) Appropriate addition of EGR is beneficial to the combustion efficiency in DMDF engine. Through inhibiting the formation of NO and shortening the conservation duration of HO2 radicals, it can reduce the NO2 emission, while the slight increase of exhaust backpressure can result in the improvement of total NOx emissions.

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