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An investigation on the characteristics of and influence factors for NO_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_2) emission, compared with conventional diesel mode. However, the detailed formation process and influence factors of NO_2 in Diesel/Methanol Dual Fuel (DMDF) engine have not been reported previously. In order to investigate the mechanism of increased NO_2 and effect factors of NO_2 emission, following works were conducted: Firstly, in light of the literature researches, a hypothesis concerning the NO_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_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_2, and the impact of temperature on the NO_2 emission mainly lay in that of temperature on hydroperoxyl (HO_2) radicals. The experiments showed that along with the increase of MSP, NO_2 emission increased firstly and then decreases. The addition of EGR could lead to the reduction of NO_2, while the slight increase of exhaust backpressure would increase total nitrogen oxides (NO_X) emission.

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 one of the research hotspots to reduce noxious emissions, have 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_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_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_2 emission, which led to the higher NO_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_2 emission. Methanol fumigation increased the NO_2 emission considerably, while the NO_2 emission in methanol emulsified mode was same as that in the biodiesel case. They asserted that the increase of NO_2 lay in the hydroperoxyl (HO_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_2 emission increased gradually, where they held the viewpoint that the cooling effect of ethanol was responsible for the increase of NO_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_2 emission

Abbreviations: DMCC, diesel/methanol compound combustion; NO_2, nitrogen dioxide; DMDF, diesel methanol dual fuel; MSP, methanol substitution proportion; HO_2, hydroperoxyl; NO_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 HO_2 free radical both contributed to the increase of NO_2.

Although being a kind of the gas pollutant for our environment, NO_2 has great research value in after-treatment system. For instance, NO_2 plays an important role in the passive regeneration of diesel particulate filter (DPF) [14], due to its strong oxidation characteristics. And the NO_2/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 NO_2 emission in fumigation approach of oxygenated fuel will be crucial. However, previous researches merely point out the possible relations of HO_2 radicals and temperature to the NO_2 formation without elaborating on the formation process and effect details when adding oxygenated fuel to diesel engine. In this paper, a hypothesis of NO_2 formation in DMDF engine was presented and validated with simulation approach. Besides, in order to explore the influence factors of NO_2 emission in the same engine, the effects of MSR, EGR and exhaust backpressure on the NO_2 emission were investigated with experiment.

2. Characteristics of NO_2 formation in DMDF engine

2.1. NO_2 mechanism

NO_2 mechanism mainly contains NO_2 formation mechanism and dissociation mechanism, which have been widely investigated [16–20]. The formation mechanism widely accepted is when touched by HO_2 radicals, the NO formed in the flame zone can be rapidly converted to NO_2 via the reaction: $NO + HO_2 \rightarrow NO_2 + OH$ [16,17], and the formation of NO_2 is mainly affected by the mixture temperature and concentration of NO and HO_2. It should be noticed that when the combustion temperature reaches the threshold value, which is usually 1200 K, the HO_2 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 HO_2 will increase rapidly [21].

On the other hand, the NO_2 can also be converted to NO via the reaction: $NO_2 + O \rightarrow NO + O_2$, and $NO_2 + H \rightarrow NO + OH$ [17,22]. An widely accepted outlook concerning NO_2 destruction is when the NO_2 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 NO_2/NO ratio [17].

2.2. Computational model

To uncover the characteristics of NO_2 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 (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 NO_X 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 NO_X mechanism in this paper was added from GRI3.0 [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].

Table 1
Parameters of the engine.

Parameters	Value
Number of cylinders	Four in-line
Displacement	4.214 L
Bore × stoke	108 × 115 mm
Compression ratio	17:1
Maximum power	103 kW@1600 r/min
Piston geometry	ω type
Inlet valve closing	−130.3 °CA ATDC
Exhaust valve opening	112.2°CA ATDC
Injection pressure	28 MPa
Nozzle (number × bore diameter)	7 × 0.16 mm

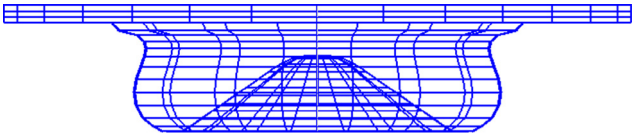

Fig. 1. Computational mesh of engine simulations.

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

$$\sum_{j=1}^{J} \nu'_{ji}\chi_j \Leftrightarrow \sum_{j=1}^{J} \nu''_{ji}\chi_j \quad \text{for } i = 1, 2, \ldots, I \tag{1}$$

where ν'_{ji} and ν''_{ji} are the stoichiometric coefficients for the reactants and products, respectively, for species j and reaction i, and χ_j represents the chemical symbol for species j. The net production rate of species j is given by:

$$\dot{\omega}_j = \sum_{i=1}^{I} \nu_{ji} q_i \quad \text{for } j = 1, 2, \ldots, J \tag{2}$$

where

$$\nu_{ji} = \nu''_{ji} - \nu'_{ji} \tag{3}$$

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

$$q_i = k_{fi} \prod_{j=1}^{J} [X_j]^{\nu'_{ji}} - k_{ri} \prod_{j=1}^{J} [X_j]^{\nu''_{ji}} \tag{4}$$

where $[X_j]$ is the molar concentration of species j, and k_{fi} and k_{ri} 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_{ci}:

$$k_{ri} = \frac{k_{fi}}{K_{ci}} \tag{5}$$

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.

2.3. Hypothesis of NO_2 formation in DMDF engine and its demonstration

2.3.1. Hypothesis of NO_2 formation in DMDF engine

According to the previous researches, there are obviously differences in NO_2 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