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CHARACTERISTICS OF NITROGEN DIOXIDE FROM A DIESEL METHANOL DUAL FUEL ENGINE

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ABSTRACT

The application of diesel methanol dual fuel (DMDF) technology to diesel engines reduces nitrogen oxides (NO_X) and particulate matter (PM) emissions, but increases hydrocarbons (HC), carbon monoxide (CO) and nitrogen dioxide (NO_2) emissions in exhaust gas. The traditional diesel oxidation catalyst (DOC) under DMDF mode has the function to simultaneously reduce HC and CO, as well as to make NO_2 be converted to nitrogen monoxide (NO). The modified DOC in this study is used to achieve high NO_2 emission, which is favor for oxidation of carbon deposited on diesel particulate filter (DPF), and to improve its activity at low temperatures. All the tests were carried out on the DMDF engine bench. The effect of the property of DOC, the methanol substitution ratio (MSR), the DOC inlet temperature and the methanol dosing on the various emissions and temperature in cs16exhaust gas was studied. Results show that the addition of CeO_2-ZrO_2-La_2O_3-Pr_2O_3 promoters to DOC facilitates the formation of NO_2 and improves its low-temperature activity. The NO_2 emission and the NO_2/NO_X increase as the MSR increases with the DOC inlet temperature from 170°C to 280°C. Compared to pure diesel mode, the high NO_2/PM ratio after the DOC at DMDF mode means that the performance of passive regeneration for DPF can be improved. Meantime, the high exhaust temperature downstream of the DOC at DMDF mode is beneficial for the passive regeneration. But the temperature-rise of exhaust at DMDF mode is limited at high loads. The DMDF mode at low loads can improve the fuel economy caused by the active regeneration.

Keywords: diesel methanol dual fuel engine, diesel oxidation catalysts, nitrogen dioxide, exhaust temperature

1. INTRODUCTION

The diesel methanol dual fuel (DMDF) technology has been applied on diesel engines to reduce the diesel consumption as well as the emissions of nitrogen oxides (NO_X) and particulate matter (PM) in the past years [1, 2]. But the DMDF mode has high hydrocarbons (HC), carbon monoxide (CO) and nitrogen dioxide (NO_2) emissions [1, 3]. The diesel oxidation catalyst (DOC) from the market effectively reduces the HC, CO and NO_2 emissions at DMDF mode [3]. But the decrease of NO_2 downstream of the DOC is bad for the passive regeneration of diesel particulate filter (DPF) [4]. Moreover, the DOC, as a heating device, increases the DPF inlet temperature in active regeneration [5]. The catalytic activity of DOC to oxidize HC injected into exhaust gas is critical, especially at low temperatures. Hence, the property of DOC is vital to affect the formation of NO_2 and the low-temperature activity. The rare earth metals, such as cerium (Ce), praseodymium (Pr) and lanthanum (La), improve the activity of DOC, especially at low temperatures [6, 7]. Triana et al. [8] found that the performance of passive regeneration was superior with the DOC inlet temperature from 363°C to 500°C. The high temperatures (>500°C) reduced the NO_2 concentration produced by DOC; and the low temperatures (<363°C) decreased the NO_2/PM. Hence, the DOC inlet temperature is a key factor in the passive regeneration. Previous studies [1, 3] mainly focused on the effect of DOC and methanol substitution ratio (MSR) on the HC, CO and NO_2 emissions, and did not involve the NO_2/PM. In addition, the effect of the DOC inlet temperature and MSR on the catalytic activity and the thermal characteristics of DOC has little been reported on DMDF engines. In this study, we chose the injection of methanol downstream of the exhaust stream (defined as methanol dosing) to provide the energy required for the active regeneration of DPF.

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In this research, the effect of the property of DOC, the MSR and the DOC inlet temperature on the emissions and temperature of exhaust was studied. Furthermore, the effect of methanol dosing on exhaust temperature and NO_2 emission was researched.

2. EXPERIMENTAL APPARATUS AND METHODS

The tests were carried out on a DMDF engine. The modification of DMDF engine has been described in ref [2]. The main parameters of this engine have also been shown in ref [2]. Figure 1 illustrates the schematic diagram of engine test system. A gas analyzer (7100DEGR, Horiba Mexa) was used to measure HC and CO emissions. NO and NO_2 emissions were measured with a gas analyzer (6000FT, Horiba Mexa). The PM emissions were attained by a smoke meter (415S, AVL Inc.). The fuels used in the tests were CHN 5 diesel fuel (the mass fraction of sulfur was under 10 ppm) and methanol (purity was 99.5 %). The physicochemical properties of diesel and methanol fuels have been shown in ref [2]. Table 1 shows the technical features of DOC.

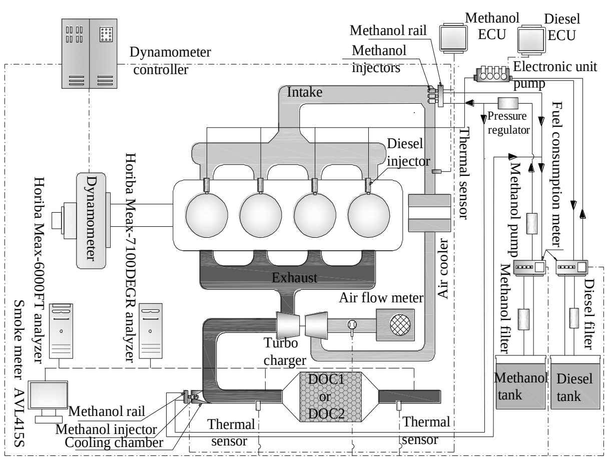

Figure 1. Schematic diagram of engine bench

Table 1. Main technical features of DOC

Feature	DOC1	DOC2
Substrate and structure	Cordierite honeycomb	Cordierite honeycomb
Coated weight (g/L)	2.12	2.12
Precious metal and ratio	Pt:Pd=1:5	Pt:Pd=1:5
Catalytic promoter	-	CeO_2-ZrO_2-La_2O_3-Pr_2O_3
CPSI	400	400
Diameter × length (mm)	190×152.4	190×152.4

In order to study the percentage of methanol used in the DMDF mode, the MSR is used and defined as the following formula (1):

$$MSR = \frac{q_d - q_{m,d}}{q_d} \times 100\ \% \qquad (1)$$

where q_d (kg/h) and $q_{m,d}$ (kg/h) are the consumption of diesel fuel on the pure diesel and DMDF modes, respectively. In the tests, the torque increased from 40 to 440 Nm with an interval of 40 Nm to achieve a gradual increase in the DOC inlet temperature. The speed was fixed at 1660 rpm. The MSR increased from 0 to the maximum. The maximum MSR (defined as MSRmax) was primarily restricted by the misfire and knock at each torque point. The methanol dosing was controlled by a methanol injector installed in exhaust pipe.

3. RESULTS AND DISCUSSION

3.1 property of DOC

Figure 2 shows the effect of DOC inlet temperature on NO_2 emission at MSR0 (Fig. 2a) and MSRmax (Fig.2b). In Fig. 2a, the NO_2 emission increases first and then decreases with the increase of DOC inlet temperature at any given DOC. The NO_2 peak concentration is mainly due to the thermodynamic equilibrium of NO conversion [9]. The NO_2 emission of DOC2 is higher than that of DOC1 at any given inlet temperature. In Fig. 2b, the NO_2 emission of DOC2 is significantly higher than that of DOC1. The NO_2 emission from the cylinder at MSRmax is higher than that at MSR0, which is due to the presence of methanol premixing zone in the cylinder under DMDF mode [10]. At any given MSR, The DOC2 facilitates the formation of NO_2 compared to DOC1, which is mainly caused by the catalytic promoters of CeO_2-ZrO_2-La_2O_3-Pr_2O_3 [6, 7].

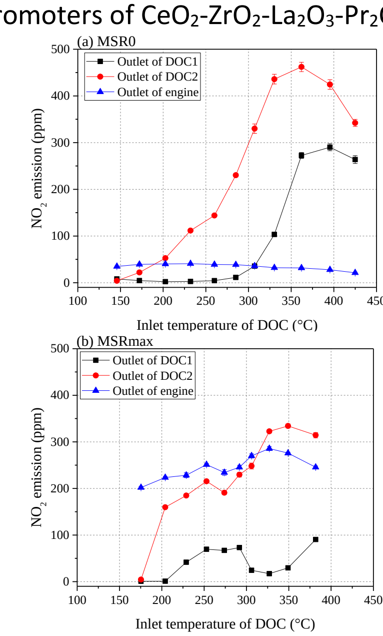

Figure 2. Effect of DOC inlet temperature on NO_2 emission at two kinds of MSRs:(a) MSR0 and (b) MSRmax

3.2 Effect of the MSR, the DOC inlet temperature and the methanol dosing on exhaust emissions and exhaust temperature

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Figure 3 shows the effect of DOC inlet temperature on the emissions of NO_2 (a) and PM (b) at three kinds of MSRs. Figure 4 displays the effect of DOC inlet temperature on the NO_2/NO_X (a) and NO_2/PM (b) at three kinds of MSRs. The DOC2 was used to test in this section. In Figs 3a and 4a, the NO_2 emission and the NO_2/NO_X downstream of the DOC reduce as the MSR increases, when the DOC inlet temperature is lower than 170°C. When the temperature is in the range of 170°C - 280°C, the NO_2 emission and the NO_2/NO_X downstream of the DOC rise as the MSR increases. When the temperature exceeds 280°C, the NO_2 emission and the NO_2/NO_X downstream of the DOC reduce as the MSR increases. In Fig. 3b, the PM emissions both before and after the DOC decrease as the MSR increases. The DOC can decrease the PM emissions. Meantime, the DMDF mode with a high MSR can effectively reduce PM emissions [2]. In Fig. 4b, the NO_2/PM downstream of DOC increases as MSR increases at any given inlet temperature. The NO_2 emission, NO_2/NO_X and NO_2/PM downstream of the DOC are higher than that upstream of the DOC, except the temperature below 270°C under DMDF mode and the temperature below 170°C under pure diesel mode. Compared to pure diesel mode, the high NO_2/PM at DMDF mode means that the good performance of passive regeneration can be achieved [4, 8, 9]. Figure 5 shows the effect of torques on the temperature both before and after the DOC at three kinds of MSRs. In Fig. 5, the temperature before the DOC slightly decreases and the temperature after the DOC significantly increases with the increase of MSR at any given torque. The decrease of temperature before the DOC at DMDF mode is mainly caused by the high latent heat of vaporization of methanol. While the temperature-rise of exhaust through the DOC at DMDF mode is due to the heat released from the total oxidation of lots of CO and HC emissions. The high exhaust temperature downstream of the DOC at DMDF mode is beneficial to the passive regeneration of DPF. But the level of temperature-rise reduces as the torque increases, which is caused by the decrease of HC and CO emissions (not shown) and the increase of heat losses [9]. Figure 6 shows the effect of methanol dosing on the exhaust temperature at three kinds of MSRs under two different torques. A temperature of 550°C downstream of the DOC was considered as the initial threshold for active regeneration in tests. In Fig. 6a, the temperature after the DOC rises as the MSR increases at any given methanol dosing. The methanol dosing required to reach the regeneration threshold is reduced by 42% when the MSR increases from 0 to 40%. In Fig. 6b, the temperature after the DOC has a little change as the MSR increases. In conclusion, the DMDF mode at low loads can improve the fuel economy caused by the active regeneration, which is due to the decrease of methanol dosing. In Fig. 7a, at low loads, NO_2 emission after the DOC at MSR0 first increases and reduces, while that at DMDF mode reduces as methanol dosing increases. In Fig. 7b, at high loads, NO_2 emission reduces as methanol dosing increases at any given MSR. It is because that high temperatures inhibit the conversion of NO to NO_2.

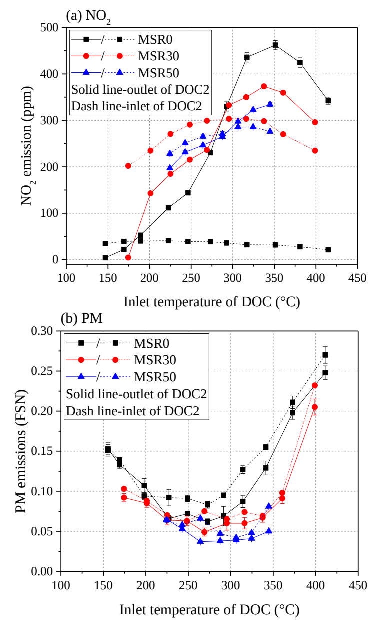

Figure 3. Effect of DOC inlet temperature on the emissions of NO_2 (a) and PM (b) at three kinds of MSRs

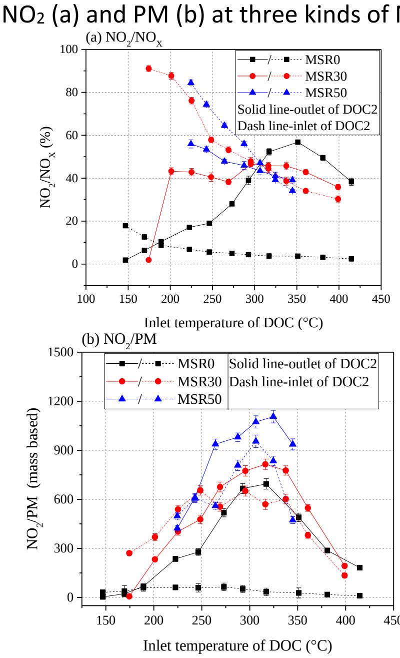

Figure 4. Effect of DOC inlet temperature on the NO_2/NO_X (a) and NO_2/PM (b) at three kinds of MSRs

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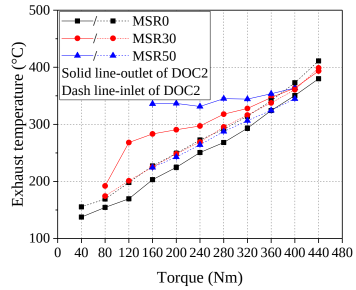

Figure 5. Effect of torques on the temperature both before and after the DOC at three kinds of MSRs

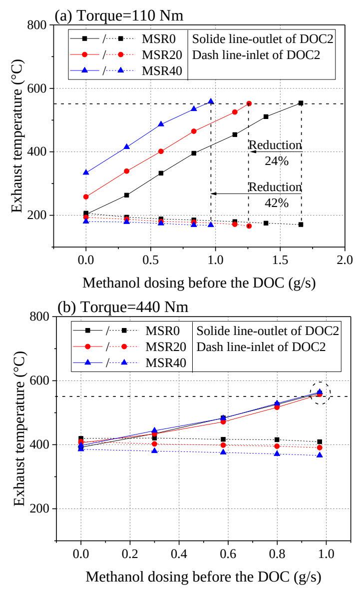

Figure 6. Effect of methanol dosing on the exhaust temperature at three kinds of MSRs under two different torques: (a) 110 Nm and (b) 440 Nm

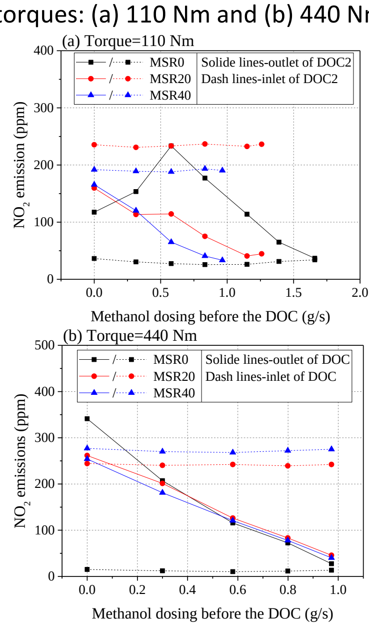

Figure 7. Effect of methanol dosing on NO_2 emission at three kinds of MSRs under two different torques: (a) 110 Nm and (b) 440 Nm

4. CONCLUSION

The effect of the property of DOC, the MSR, the DOC inlet temperature and the methanol dosing on the various emissions and temperature in exhaust gas was studied in a DMDF engine. The main findings are summarized as follows: the addition of CeO_2-ZrO_2-La_2O_3-Pr_2O_3 promoters to DOC facilitates the formation of NO_2 at any given MSR. The DOC inlet temperature and the MSR influence the NO_2 emission and the NO_2/NO_X. The NO_2 emission and NO_2/NO_X increase as the MSR increases with the DOC inlet temperature from 170°C to 280°C. Compared to pure diesel mode, the high NO_2/PM downstream of the DOC at DMDF mode means that the performance of passive regeneration can be improved. Meantime, the high exhaust temperature downstream of the DOC at DMDF mode is beneficial for the passive regeneration of DPF. But the temperature-rise of exhaust at DMDF mode is limited at high loads. The methanol dosing increases the DOC outlet temperatures, but reduces NO_2 emission after the DOC, except the case that diesel mode at low loads. The DMDF mode at low loads can improve the fuel economy caused by the active regeneration, which is due to the decrease of methanol dosing.

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