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ARTICLE *in* ENERGY & FUELS · NOVEMBER 2009

Impact Factor: 2.79 · DOI: 10.1021/ef9005516

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Energy Fuels **XXXX,** *XXX,* 000–000 · DOI:10.1021/ef9005516

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Investigation on the Effect of Port-Injected Methanol on the Performance and Emissions of a Diesel Engine at Different Engine Speeds

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Received May 29, 2009. Revised Manuscript Received July 22, 2009

This study is aimed at investigating the effect of port-injected methanol on the performance and emissions of a diesel engine under different engine loads and engine speeds. Experiments were performed on a four-cylinder diesel engine operating at three engine speeds and five engine loads for each speed. The results show that when methanol is injected into the intake port of the diesel engine, the brake thermal efficiency decreases at low engine loads but has no significant change at medium to high engine loads. There is also a reduction of NO_x and particulates but a significant increase in CO, HC, NO_2, unburned methanol, and formaldehyde emissions. The application of port-injected methanol shows potential greenhouse benefits only at high engine loads with a high level of fumigation methanol. With a diesel oxidation catalyst, the HC, CO, unburned methanol, and formaldehyde emissions are significantly reduced when the exhaust gas temperature is sufficiently high. The results are consistent at each engine speed.

1. Introduction

Diesel vehicles are one of the major sources of respirable suspended particulates and nitrogen oxides (NO_x), which are threats to human health. One of the approaches to reduce these pollutants emitted from diesel vehicles is to use alternative fuels to partly or totally replace the diesel fuel. The favorable alternative fuels should be abundant, cheap to compete with diesel fuel, easily applied to a diesel engine, and able to improve exhaust emissions. Methanol is a suitable choice. It can be readily converted from natural gas or synthesized from coal, municipal wastes, and biomass.[1,2] Producing methanol from coal is especially important to those countries, like China, which are rich in coal but poor in oil reserves. Methanol has high oxygen content and high H/C ratio, which are beneficial for improving combustion and reducing the formation of soot. Moreover, methanol has a much higher latent heat of vaporization than the diesel fuel, which can lead to a cooling effect on the cylinder charge and hence a reduction of NO_x emission.[3]

There are several approaches for applying methanol to a diesel engine. First, methanol alone or methanol with ignition-improver can be burned in a diesel engine with or without ignition aids. This method has received active research in the 1980s and the early 1990s, leading to the introduction of methanol-fueled buses in New York and in Los Angeles.[4−6] However, the development of methanol-fueled vehicles had slowed down in the late 1990s due to the operational problems associated with these vehicles. Second, methanol can be mixed with diesel fuel and a stabilization additive. The blended fuel can be applied to a diesel engine with no need to modify the engine. However, there is a limitation on the amount of methanol that can be mixed with diesel fuel for stable operation. Moreover, the amount of methanol mixed with the diesel fuel cannot be varied during engine operation.[3,7−9] Third, methanol can be applied by injecting it into the air intake of a diesel engine using low-pressure fuel injectors. This approach is called the fumigation method, which requires minor modification of the diesel engine. This approach allows a larger percentage of methanol to be used, subjected to the limitation of engine knocking. The fumigation method has been investigated by Popa et al.,[10] Udayakumar et al.,[11] Yao et al.,[12,13] Cheng et al.,[14] and Song et al.[15] Cheng et al.[14] performed investigation on a four-cylinder diesel engine and found reductions in NO_x and PM emissions but significant increase in HC and CO emissions. Similar results were also obtained by

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Song et al.,[15] who carried out investigations on a single-cylinder diesel engine.

The fumigation method seems to be more flexible despite an extra fuel injection system being required. It can allow the amount of injected methanol to vary depending on actual requirements. Moreover, since the methanol is not premixed with the diesel fuel, industrial grade methanol that is at a lower cost can be used. Yao et al.[12,13] proposed to run the diesel engine on diesel fuel alone at engine start and light engine load to ensure cold-starting capability and avoid excess HC and CO emissions; and to run in the fumigation mode at medium and high engine loads to reduce smoke and NO_x emissions. However, the detailed engine control strategy and the influence of the mass fraction of methanol on engine emissions have not yet been fully investigated. Former investigations were mainly carried out at a single engine speed while in actual operation a diesel engine is required to operate at different engine speeds. Moreover, although some investigations have been carried out on the regulated emissions from the methanol fumigated diesel engine, more attention should be given to the unregulated emissions that are more toxic. In this paper, two unregulated emissions that are commonly found in methanol-fueled engines, namely, unburned methanol and formaldehyde, are also investigated.

The present study is aimed to provide further experimental data on the effect of fumigation methanol on the engine emissions and the sensitivity of these emissions to the amount of fumigation methanol applied under different engine loads and engine speeds. Besides the regulated emissions, the unburned methanol and formaldehyde emissions were measured. In addition, the effect of a diesel oxidation catalyst (DOC) on reducing the regulated and unregulated emissions was also investigated. Euro V diesel fuel containing less than 10 ppm wt of sulfur was used in this study, whereas in former investigations the fuel sulfur contents are either not mentioned or are much higher than the one used in this study.

2. Experimental Section

2.1. Test Engine and Fuels. A naturally aspirated, four-cylinder direct-injection diesel engine with specifications shown in Table 1 was used for the experiments. The engine was coupled with an eddy-current dynamometer, and the engine speed and torque were controlled by the Ono Sokki diesel engine test system. A methanol fuel rail and four fuel injectors were added to the inlet manifold of the engine. A fuel pump was used to inject methanol into the intake manifold at a pressure of 0.35 MPa to form a lean homogeneous methanol/air mixture. An electronic control unit was used to control the amount of methanol injected into the air intake by adjusting the width of the injection pulse. An Engelhard CCX8772A DOC was installed at the downstream end, 850 mm from the exhaust manifold, to further reduce the pollutants in the exhaust gas. Two valves were added into the exhaust pipe so that the exhaust gas before and after the DOC can be investigated by switching the valves. A K-type thermocouple was used to measure the exhaust gas temperature before the DOC. The experimental setup is shown in Figure 1.

The fuels used include Euro V diesel fuel with less than 10 ppm by weight of sulfur and industrial grade methanol. Major properties of the fuels are shown in Table 2. Fuel consumptions were measured using an electronic balance with a precision of 0.1 g.

2.2. Sampling and Analysis. The major measuring instruments used in this study are given in Table 3. Regulated gaseous emissions including CO, CO_2, HC, and NOx/NO were measured online using exhaust gas analyzers. HC was measured with a heated flame ionization detector (HFID); NOx/NO was measured with a heated chemiluminescent analyzer (HCLA); and CO and CO_2 were measured with nondispersive infrared analyzers (NDIR). All gas analyzers were calibrated with standard gases and zero gas before each experiment. Unregulated gaseous emissions including unburned methanol and formaldehyde were online analyzed with the Airsense multichannel gas analyzer. The analyzer is an ion molecule reaction (IMR) mass spectrometer. The detection principle of the instrument is based on the analysis of the molecular weight of the gas species. The instrument uses electron ionization to create a primary ion beam of mercury, xenon, or krypton. Sample gas is introduced to a high vacuum chamber and transformed by the primary ion beam into ions that are subsequently mass selected by electromagnetic fields and counted in a particle counter. Further information about the instrument and the calibration can be found in Villinger et al.[16,17] and Dearth.[18] The gas sample was

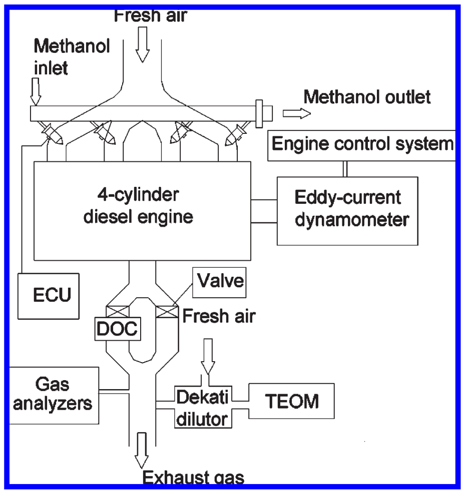

Figure 1. Schematic of experimental system.

Table 1. Specifications of the Test Engine

model	Isuzu 4HF1
type	in-line, four-cylinder, direct injection
maximum power	88/3200 (kW/rpm)
maximum torque	285/1800 (Nm/rpm)
bore/stroke (mm)	112/110
displacement (cm^3)	4334
compression ratio	19.0:1

Table 2. Properties of Euro V Diesel Fuel and Methanol[3,14]

properties	Euro V diesel	methanol
Molecular formula		CH_30H
Molecular weight, g/mol		32
Stoichiometric fuel/air ratio	< 0.1	0.15
Cetane number	> 51	< 5
Flash point, °C	78	107
Ignition temperature, °C	316	470
Viscosity at 20 °C, mPa·s	2.8	0.59
Density, kg/m^3	830	790
Lower heating value, MJ/kg	42.5	19.7
Heat of vaporization, kJ/kg	270	1178
Oxygen content, wt.%	0	50
Sulfur content, ppm wt	< 10	
Flame temperature, °C	2054	1890

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Table 3. List of Major Test Equipment

instrument	exhaust species	unit	manufacturer and type
heated flame ionization detector (HFID)	THC	ppm	CAI model 300
heated chemiluminescent analyzer (HCLA)	NO_x	ppm	CAI model 400
nondispersive infrared	CO	ppm	CAI 300
analyzer (NDIR)	CO_2	%	
multichannel gas analyzer	methanol, formaldehyde	ppm	V&F Airsense Net
TEOM	particulate mass concentration	mg/m^3	R&P TEOM1105

Table 4. Engine Test Conditions: Speed, Torque and Brake Mean Effective Pressure (BMEP)

speed/ rpm	maximum torque/ Nm	load percentage/ %	torque/ N m	power/ kW	BMEP/ MPa
1280	220	20	44	5.9	0.128
		40	88	11.8	0.255
		60	132	17.7	0.383
		80	176	23.6	0.510
		95	209	28	0.606
1920	230	20	46	9.2	0.133
		40	92	18.5	0.267
		60	138	27.7	0.400
		80	184	37	0.533
		95	218	43.8	0.632
2560	200	20	40	10.7	0.116
		40	80	21.4	0.232
		60	120	32.2	0.348
		80	160	42.9	0.464
		95	190	50.9	0.551

taken directly from the engine exhaust and maintained at 190 °C to the multicomponent gas analyzer. In this study, unburned methanol and formaldehyde were calibrated directly using standard gases. A tapered element oscillating microbalance (TEOM) was used for measuring particulate mass concentration. For each test, the exhaust gas for particle sampling was diluted by a Dekati minidiluter.

In this study, the total HC was measured with the HFID, which has weaker response to the oxygenated hydrocarbons.[19] Thus, the HC concentration reported in this paper does not reflect the true level of the oxygenated compounds, but it does include a certain contribution from the oxygenated compounds, including methanol and formaldehyde.

2.3. Test Procedure. Experiments were performed at the engine speeds of 1280, 1920, and 2560 rpm, corresponding to 40, 60, and 80% of the maximum engine speed. When the engine was operated on diesel fuel alone, the maximum attainable engine loads for smooth operation were 220, 230, and 200 N m, respectively, for the engine speeds of 1280, 1920, and 2560 rpm. Five engine loads at each engine speed, corresponding to 20, 40, 60, 80, and 95% of the maximum engine load, were selected for the study. The detailed engine loads at each speed are shown in Table 4. Experiments were first carried out using diesel fuel alone to build up a database for comparison with those obtained with fumigation methanol. Experiments were then carried out with the diesel fuel to take up 90% of the desired engine load while the rest of the desired load was taken up by fumigation methanol. Experiments were repeated with the diesel fuel taking up 80 and 70% of the desired engine load, with fumigation methanol providing 20 and 30% of the desired engine loads. Therefore, in this paper and in the figures, when we mention x% fumigation methanol or x% MeOH, we are referring to the case that fumigation methanol takes up x% of the engine load.

At each mode of operation, the engine was allowed to run for a few minutes until the exhaust gas temperature, the lubricating oil temperature, the cooling water temperature, as well as the CO_2 concentration have attained steady-state values and data were measured subsequently. All the gaseous emissions and particulate mass concentrations were continuously measured for 5 min at the exhaust tailpipe of the diesel engine and the average results are presented. Experiments were repeated twice, and the results of the three tests were found to agree with each other within the experimental uncertainties of the measurements. The experimental uncertainty and standard errors in the measurements have been determined based on the method of Kline and McClintock.[20] The experimental uncertainties at 95% level of confidence are 9.7% for HC, 6.4% for CO, 2.8% for NO_x, 7.3% for NO_2, 0.6% for CO_2, and up to 5% for unburned methanol and formaldehyde; and the standard error is 1.8% for particulate mass concentration.

3. Results and Discussion

3.1. Engine Performance. For each test, based on the engine torque, the engine speed, and the mass consumption of diesel fuel and methanol, the brake thermal efficiency (η) was calculated. The mass flow rates of the fuels, the brake thermal efficiency and the exhaust gas temperature are shown in Table 5.

As shown in Table 5, the brake thermal efficiency increases with engine load but decreases with engine speed for diesel fuel and for fumigation methanol. However, at any engine speed, the effect of fumigation methanol is load dependent. At 20 and 40% engine loads, at each engine speed, the brake thermal efficiency deceases with increasing level of fumigation methanol. At higher engine loads, the effect of fumigation level on the brake thermal efficiency becomes negligible.

The lower brake thermal efficiency at higher engine speed is due to increase in incomplete combustion, increase in mechanical frictional losses, and decrease in volumetric efficiency. The exhaust gas temperature is higher at the higher engine speed, indicating that more heat is released at a later stage of the expansion stroke.

With fumigation methanol, there are several factors affecting engine performance. First, fumigation methanol might cool down the air/fuel mixture due to its much higher latent heat of evaporation (1178 kJ/kg) compared with that of the diesel fuel (270 kJ/kg), which will contribute to a drop in the brake thermal efficiency. Second, during the valve overlap period, a small amount of unburned methanol may directly escape into the exhaust gas, which also increases the fuel consumption and reduces the brake thermal efficiency. This is also one of the reasons leading to the increase of unburned hydrocarbon and methanol emissions when the engine is operated in the fumigation mode. Third, the homogeneous air/methanol mixture burns faster, and methanol in the air/fuel charge provides additional oxygen for diffusion combustion, both of which will contribute to an increase in the brake thermal efficiency. At low engine loads, due to the low in-cylinder gas temperature, as reflected by the lower exhaust gas temperature shown in Table 5, the cooling effect, together with the leaner air/methanol mixture might

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Table 5. Mass Flow Rates of Diesel and Methanol, Brake Thermal Efficiency (η), and Exhaust Gas Temperature under Different Engine Test Conditions

		Baseline			10% MeOH				20% MeOH				30% MeOH			
speed/ rpm	load/ %	D/ kg/h	η/ %	temp/ °C	D/ kg/h	M/ kg/h	η/ %	temp/ °C	D/ kg/h	M/ kg/h	η/ %	temp/ °C	D/ kg/h	M/ kg/h	η/ %	temp/ °C
1280	20	1.98	25.3	158	1.89	0.33	24.5	154	1.78	0.72	23.7	155	1.69	1.01	23.0	158
	40	2.98	33.4	216	2.80	0.55	32.6	213	2.62	1.05	31.4	214	2.41	1.56	30.8	211
	60	4.09	36.7	282	3.73	0.79	36.6	271	3.39	1.57	36.3	275	3.06	2.36	36.1	271
	80	5.16	38.7	352	5.15	0.95	38.8	348	4.71	2.05	38.7	345	4.21	3.07	38.6	332
	95	6.01	39.5	416	5.51	1.19	39.2	406	4.93	2.45	39.1	394	4.39	3.73	38.8	384
1920	20	3.36	23.3	211	3.21	0.56	22.6	212	3.10	1.05	21.9	208	2.89	1.89	20.8	209
	40	4.81	32.6	281	4.48	0.90	32.0	271	4.18	1.88	31.1	279	4.05	2.70	29.5	280
	60	6.42	36.6	360	5.87	1.38	36.5	353	5.34	2.49	36.2	352	4.88	3.51	36.0	356
	80	8.26	38.0	452	7.57	1.63	37.6	441	6.82	3.18	37.8	436	6.09	4.85	38.0	433
	95	9.71	38.2	532	8.76	2.17	38.0	512	7.88	3.80	38.5	506	7.01	5.63	38.6	492
2560	20	4.79	19.0	266	4.60	0.74	18.4	259	4.41	1.57	17.7	264	4.28	2.26	17.1	264
	40	6.61	27.5	340	6.29	1.01	26.9	334	5.91	2.47	25.8	342	5.69	3.58	24.8	342
	60	8.57	31.8	417	8.06	1.44	31.2	413	7.31	3.25	30.9	419	6.74	4.60	30.7	419
	80	10.91	33.3	506	10.0	2.02	33.2	499	9.06	4.06	33.2	499	8.24	5.71	33.4	495
	95	12.68	34.0	591	11.59	2.39	34.1	576	10.34	4.70	34.5	564	9.14	6.84	34.3	560

result in reduced BTE with increase in fumigation methanol. At high engine loads, the in-cylinder gas temperature is higher and there is more methanol in the air/fuel charge, which tends to reduce the adverse effect on engine performance, leading to improvement in the brake thermal efficiency.[14] Song et al.[15] found that better fuel economy is obtained at high engine load and high methanol fraction. Cheng et al.[14] concluded that at low engine load, the brake thermal efficiency decreases, but at high engine load, it increases, with the fumigation methanol. From the results in the literature and this investigation, it can be concluded that there is a poor utilization of methanol at low engine loads, but the effect is positive at high engine loads.

3.2. Regulated Emissions. *3.2.1. HC and CO Emissions.* The effect of fumigation methanol on HC and CO emissions are shown in Figures 2 and 3, respectively. The HC measurement was calibrated with propane but the results are shown in ppmC_1.

Figures 2 and 3 show that under different engine speeds, the maximum HC and the maximum CO concentrations occur at either 20 or 40% engine load and then decrease with further increase of engine load. There is an obvious increase of HC and CO emissions with an increase of fumigation methanol at all engine loads and each engine speed. At each engine speed, the increase in CO emission is more significant with 10% fumigation methanol and less significant at higher level of fumigation methanol. The HC and CO emissions, averaged on different engine loads, in the fumigation mode, are more than double of those obtained with the baseline engine. The level of increase of HC and CO emissions obtained in this study is similar to the results of Yao et al.,[13] Cheng et al.,[14] and Song et al.[15] in which fumigation methanol was also applied; but much higher than those of Chao et al.,[7] Canakci et al.,[8] and Huang et al.[9] in which premixed methanol was applied. This is because, when operating in the fumigation mode, the uniform air/methanol mixture in the cylinder, coupled with the lower gas temperature, tends to form more unburned HC and CO emissions.

When operating in the fumigation mode, the air/methanol mixture tends to form unburned hydrocarbon in the same way as that occurring in a petrol engine. During the combustion process, the air/methanol mixture trapped in crevices or quenched by the cylinder wall, as well as those adsorbed by oil film, may form unburned HC, especially as the air/methanol mixture becomes richer at higher level of

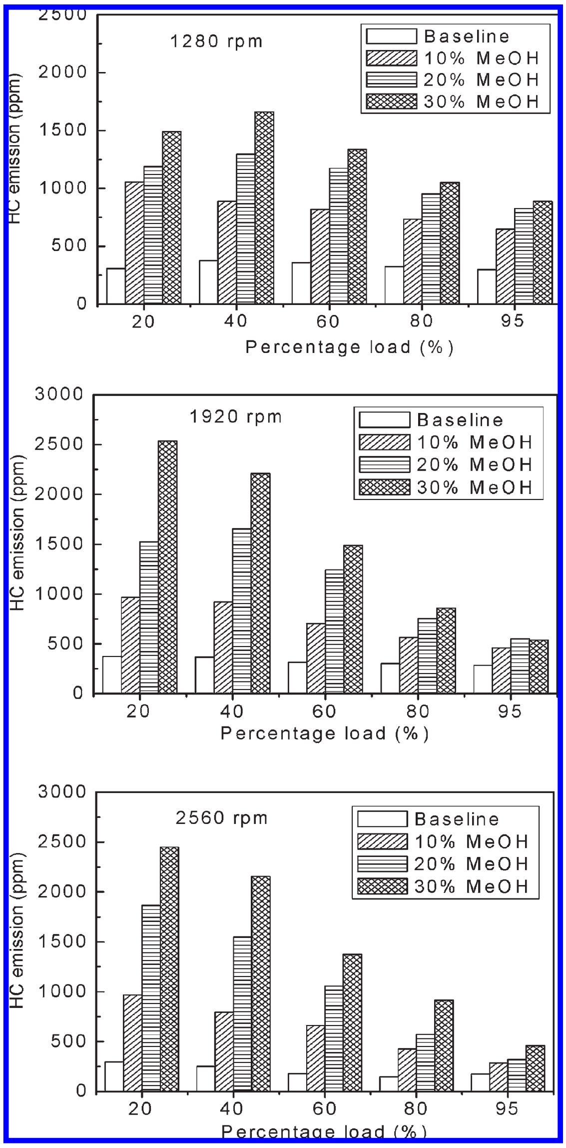

Figure 2. Effect of fumigation methanol on HC emission.

fumigation. Fumigation methanol also tends to lower the combustion temperature, which might also enhance the formation of incomplete combustion product and hence

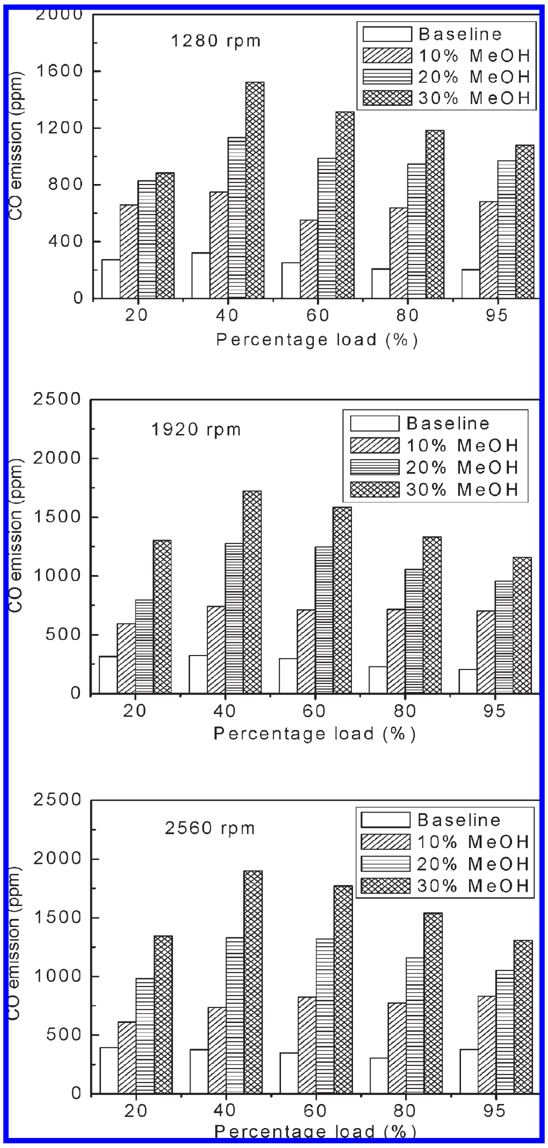

Figure 3. Effect of fumigation methanol on CO emission.

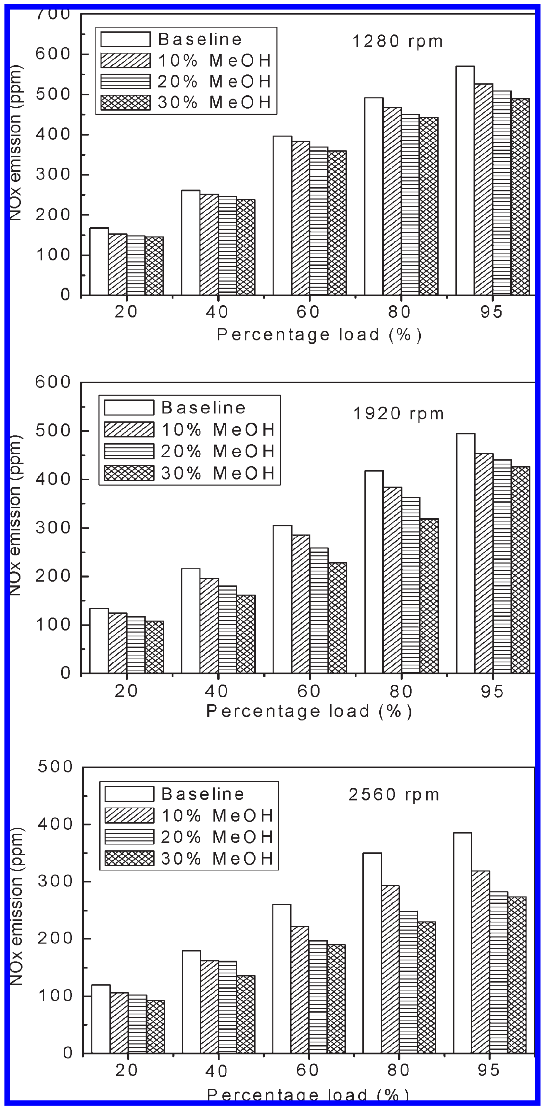

Figure 4. Effect of fumigation methanol on NO_x emission.

increase HC emissions. This tendency will be enhanced at higher fumigation ratio and lower engine load because of the lower combustion temperature.

CO emissions are expected to increase under conditions that cause incomplete combustion such as lower combustion temperature or poor mixing and are primarily controlled by the global or local air/fuel equivalence ratio.[19] In the fumigation mode, the methanol is burned as a homogeneous charge and the flame has to propagate through the charge. The lower flame temperature due to high vaporization cooling effect of methanol makes it difficult to have complete oxidation of the methanol/air mixture, resulting in an increase CO emission.

3.2.2. NO_x Emissions. Figures 4 and 5 show, respectively, the variation of NO_x and NO_2 emissions with engine load and engine speed. At each engine speed, there is an increase of NO_x emission with engine load but a decrease of it with percentage of fumigation methanol. For NO_2, its concentration increases to the maximum value at certain medium engine load and then decreases at higher engine loads.

In general, there is a reduction of NO_x emission but a significant increase of NO_2 emission when the engine is operated with fumigation methanol. Compared with diesel fuel operation, averaged on the different engine loads, the reduction in NO_x emission varies from 5.6 to 27.5% and the increase in NO_2 emission varies from 2.9 to 5.7 times, depending on the engine speed and the level of fumigation methanol. Yao et al.[12] carried out tests on two diesel engines, one naturally aspirated and the other turbocharged. Their results showed NO_x reduction of about 8% for the naturally aspirated engine and 16% for the turbocharged engine. Song et al.[15] found a reduction of NO_x emission at different engine loads and speeds. Cheng et al.[14] also reported a reduction in NO_x emission from the methanol fumigated diesel engine using ultra low sulfur diesel as the base fuel. On the basis of these results, it is obvious that the fumigation methanol leads to NO_x reduction. However, there is tremendous increase in NO_2 emission.

NO_x from diesel engine is mainly formed by the oxidation of nitrogen at high temperature. Therefore, the oxygen content and flame temperature are significant factors affecting NO_x formation. With fumigation methanol, the increase in oxygen in the fuel might enhance NO_x formation. However, the cooling effect of methanol might reduce the flame temperature and hence reduce NO_x formation. The results indicate that the cooling effect has led to the reduction in

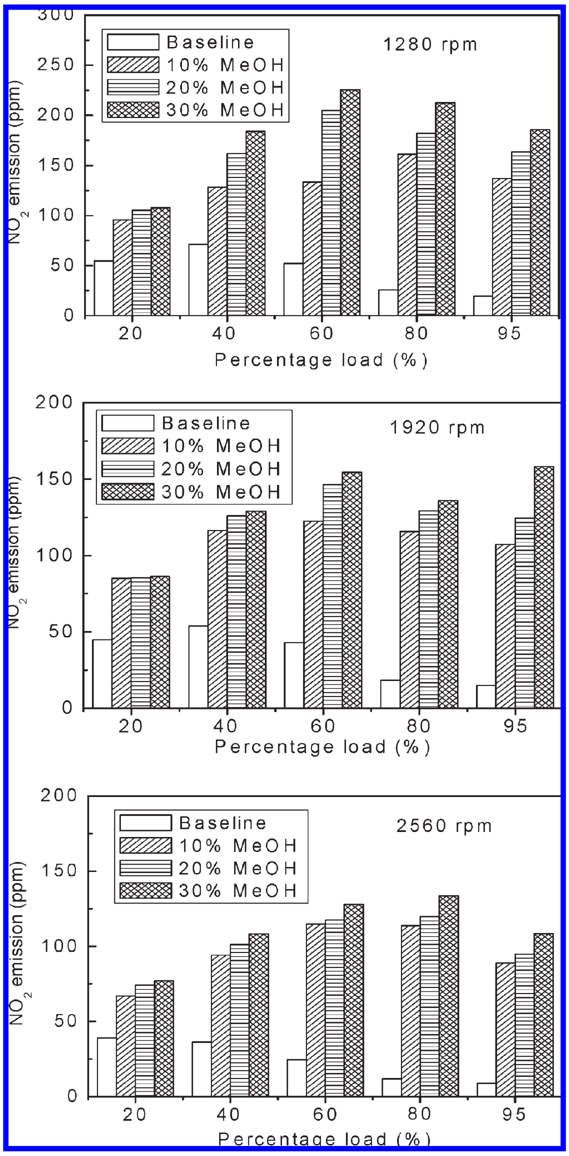

Figure 5. Effect of fumigation methanol on NO_2 emission.

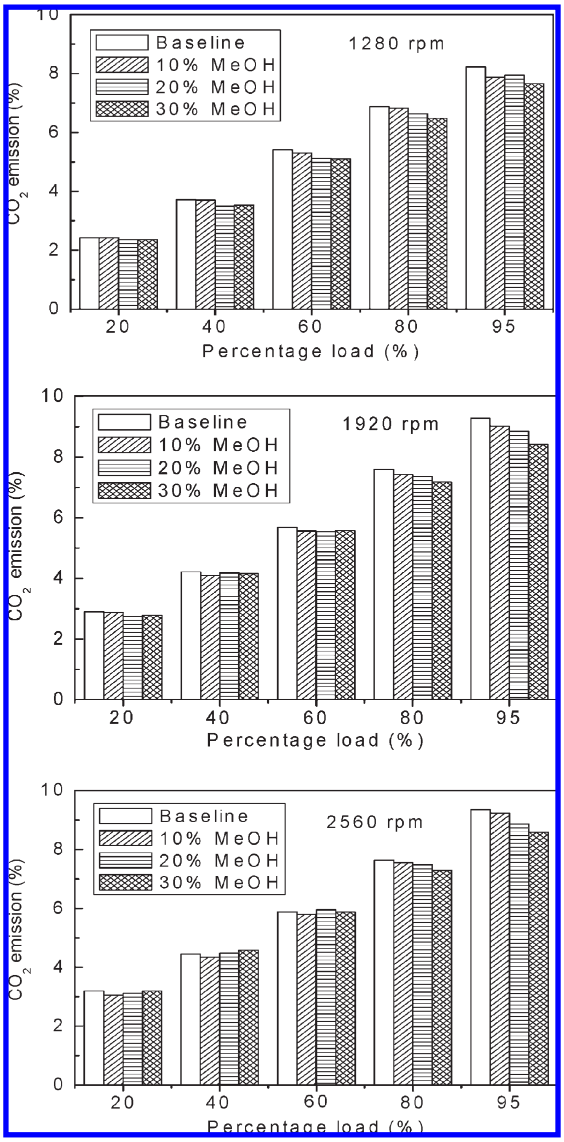

Figure 6. Effect of fumigation methanol on CO_2 emission.

NO_x emission when fumigation methanol is applied. On the other hand, Yano et al.[21] and Lyon et al.[22] showed that the oxidation of methanol in NO can lead to the formation of NO_2, with methanol functioning as a source of HO_2 free radicals. The same reason might have led to the increase of NO_2 emission in this investigation.

3.2.3. CO_2 Emission. The CO_2 emissions are shown in Figure 6. There is an increase of CO_2 emission with engine load. There is a reduction of CO_2 emission with increase in fumigation methanol at high engine loads only. Similar results are obtained at each engine speed. The results indicate that the application of fumigation methanol has greenhouse gas reduction benefits only at high engine load with high level of fumigation methanol.

The emission rate of CO_2 is affected by both the brake thermal efficiency and the properties of the fuels. When operating with fumigation methanol at low engine loads, the poorer brake thermal efficiency leads to significant increase in fuel consumption, which offsets the potential CO_2 reduction benefits of methanol. However, the higher HC and CO emissions, as shown in Figures 2 and 3, at low engine loads can partly lead to lower CO_2 emission. Thus, despite the poorer brake thermal efficiency, there is no obvious change in CO_2 emission. At high engine loads, the improvement in engine performance with fumigation methanol leads to a reduction in fuel consumption and hence reduction of CO_2. The reduction varies from 1.2 to 7.4%, depending on the engine load, engine speed, and level of fumigation methanol. Chao et al.[7] did not find any significant benefits in terms of CO_2 reduction using up to 15% by volume of blended methanol in both steady-state and transient cycle tests. Canakci et al.[8] found that CO_2 emission increased under different injection timings when methanol-blended diesel fuel was used. Cheng et al.[14] found that the mass emission rate of CO_2 increases at low engine load but do not significantly change at medium and high loads. Song et al.[15] found that CO_2 emissions increased by 7.59% at high engine load with a fumigation ratio of 40%. The results in literature are different from ours.

3.2.4. Particulate Emissions. The variation of particulate mass concentration, expressed in milligrams per cubic meter,

(21) Yano, T.; Ito, K. *Bull. Japan Soc. Mech. Eng*. **1983**, *26*, 94–101.
(22) Lyon, R. K.; Cole, J. A.; Kramlich, J. C.; Chen, S. L. *Combust. Flame* **1990**, *81*, 30–39.

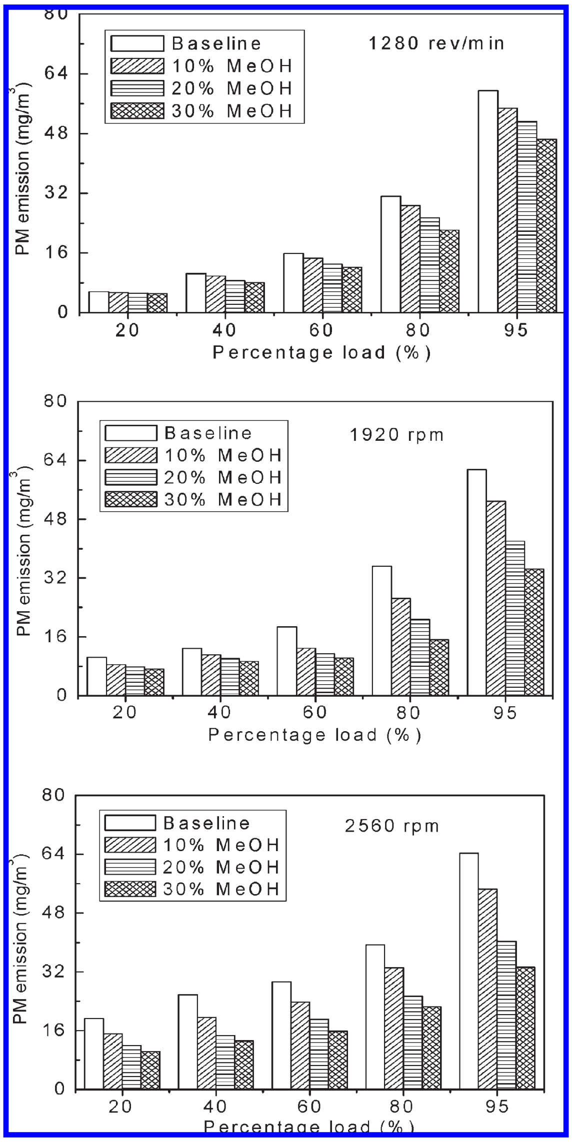

Figure 7. Effect of fumigation methanol on PM emission.

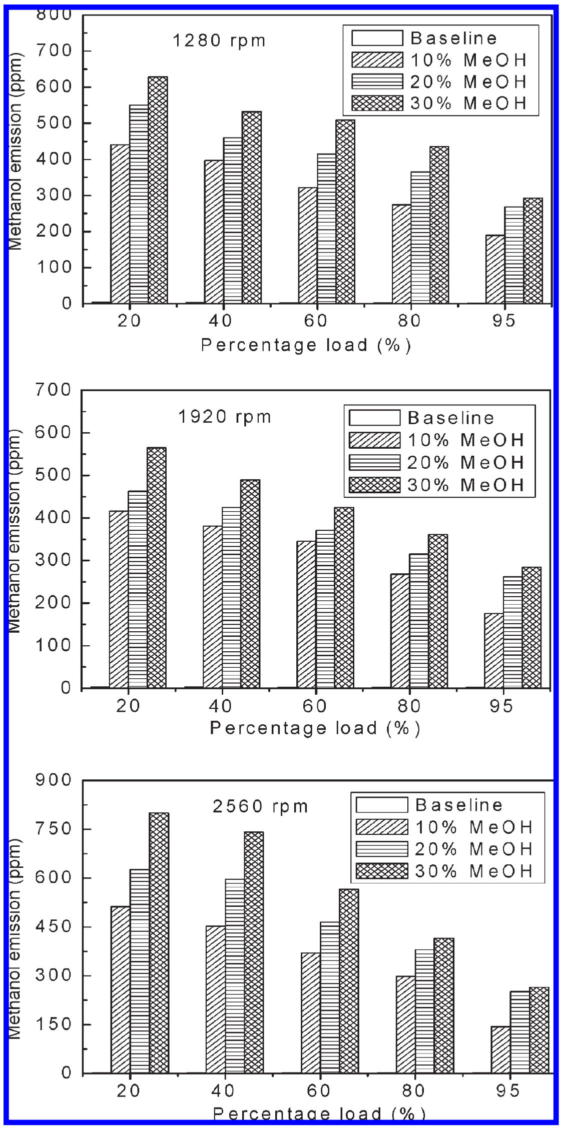

Figure 8. Effect of fumigation methanol on methanol emission.

is shown in Figure 7. In general, it increases with increase in engine load and engine speed but decreases with increase in fumigation methanol. The particulate mass concentrations are reduced by 9–23, 20–40, and 19–48% for the engine speeds of 1280, 1920, and 2560 rpm, respectively, under different levels of fumigation methanol and engine loads, compared with the baseline engine. The percentage reduction increases with the percentage of fumigation methanol applied. Cheng et al.[14] obtained similar results. They found a maximum reduction of 49% in particulate mass concentration when operating on ultra low sulfur diesel with 30% fumigation methanol at an engine speed of 1800 rpm.

PM consists mainly of combustion-generated carbonaceous soot on which some organic or hydrocarbon compounds and sulfates have been adsorbed. Carbonaceous soot is formed in the center of the fuel spray where the air/fuel ratio is low. With fumigation methanol, at the same engine load, less diesel fuel is burned in a mixture of methanol and air, thus less soot and hence less particulate is formed. The amount of diesel fuel consumed decreases with increase in the percentage of fumigation methanol, leading to a decrease of particulate emission with increase of percentage of fumigation methanol. Furthermore, methanol is sulfur free, contains no aromatic contents, and has lower C/H mass ratio, all of which can help in reducing PM formation. On the other hand, the soluble organic fraction (SOF) may increase with the level of fumigation methanol. The results of this study show that there is a net reduction in particulate mass concentration, indicating that the reduction in soot and sulfate is more than the increase of SOF in the diesel particulate.

3.3. Unregulated Emissions. *3.3.1. Unburned Methanol Emissions*. As shown in Figure 8, the unburned methanol concentration in the exhaust gas is very low with the diesel fuel. When fumigation methanol is applied, there is a surge of the unburned methanol concentration. However, it decreases with increase of engine load. Similar results are obtained at each engine speed. The significant increase of unburned methanol leads to a corresponding increase of the unburned hydrocarbon in the engine exhaust. Kim and Foster[23] carried

(23) Kim, C.; Foster, D. E. Aldehyde and unburned fuel emission measurements from a methanol-fueled Texaco stratified charge engine. *SAE Paper 852120*, 1985.

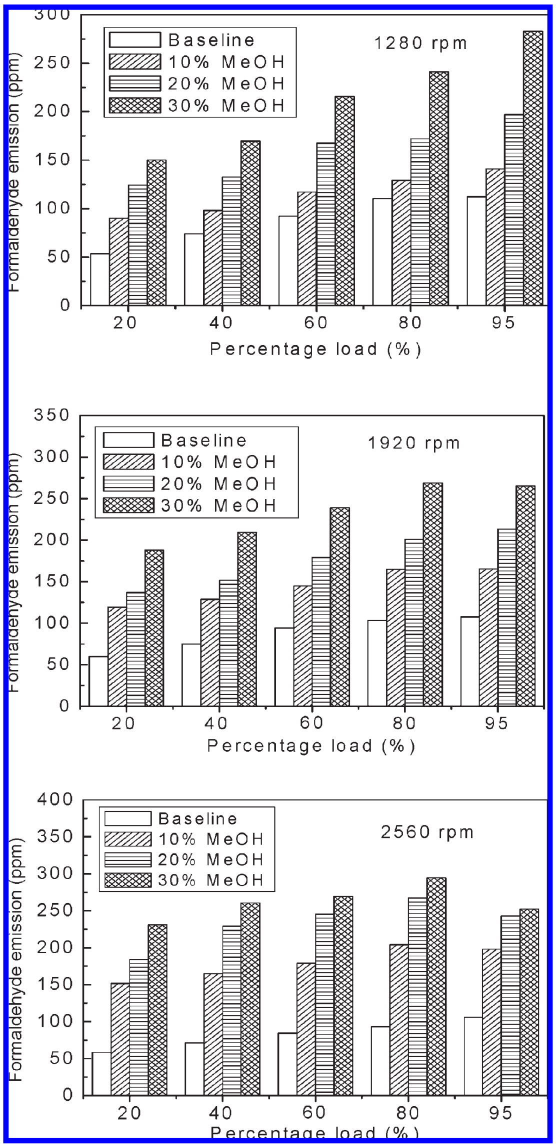

Figure 9. Effect of fumigation methanol on formaldehyde emission.

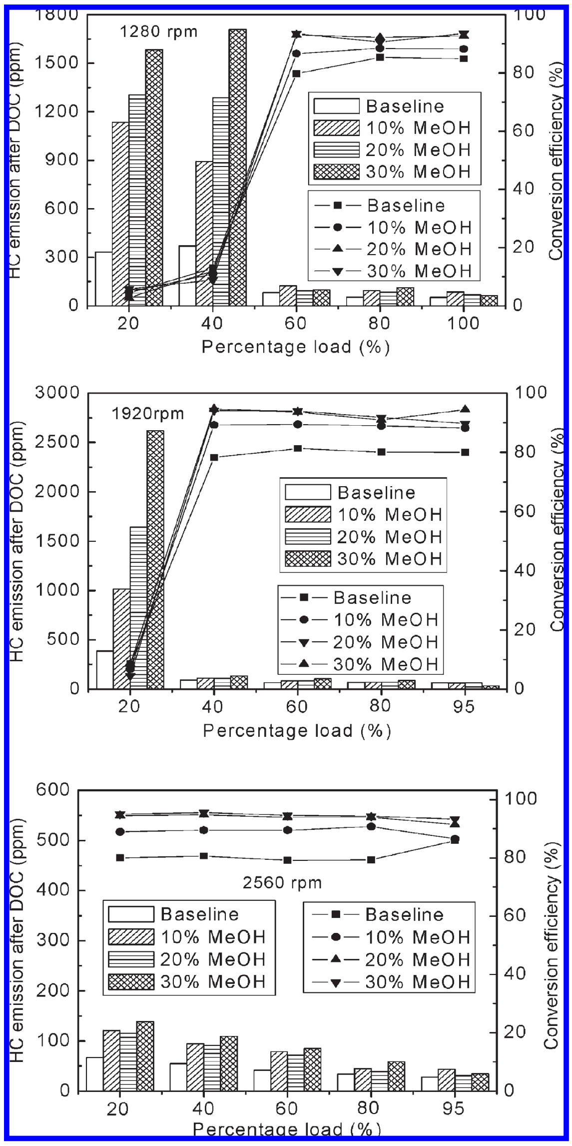

Figure 10. HC emission and conversion efficiency after DOC.

out study on a methanol-fueled Texaco stratified charge engine. Their results show that increasing engine load results in a decrease of the unburned methanol emission but engine speed has little effect on methanol emission. Lipair and Keski-Hynnila[24] measured the unburned methanol emission from a methanol-fueled heavy-duty diesel engine with the 13-mode test cycle and found that the unburned methanol emission is the highest in the idle mode and decreases with increasing engine speed and engine load.

There are two sources of methanol in the engine exhaust. One is the intermediate product from the diesel combustion and the other is from the fumigation methanol. The results show that methanol emission is less than 5 ppm for diesel-only operation but it increases to several hundred ppm when fumigation methanol is applied. This is an indication that the methanol in the exhaust comes from the fumigation methanol which has escaped combustion. There are several factors affecting the unburned methanol emission under different engine operating conditions and different levels of fumigation methanol. The methanol/air mixture might be too lean to support combustion at low engine loads. Bulk quenching and lack of post flame oxidation also contributes to the high methanol emission at low engine load, as well as at other engine loads. Methanol entrapped near the cylinder head is another source of methanol emissions.[23] The methanol emissions from these sources are higher at low engine load because of the low combustion temperature; and lower at high engine load, at which the combustion temperature should be much higher.

A comparison of the HC and methanol emissions indicates that the increase of HC is much higher than the methanol emissions. Thus, the fumigation methanol leads to an increase of unburned methanol, as well as other hydrocarbons, especially at low engine loads.

3.3.2. Formaldehyde Emission. As shown in Figure 9, in general, there is an increase in formaldehyde emission with increase in engine load and fumigation methanol. Compared with diesel fuel operation, averaged on the different engine loads, the formaldehyde emissions are 1.3−2.4, 1.7−2.7, and 2.2−3.3 times higher, respectively, for the engine

(24) Lipari, F.; Keski-hynnila, D. Aldehyde and unburned fuel emissions from methanol-fueled heavy-duty diesel engines. *SAE Paper 860307*, 1986.

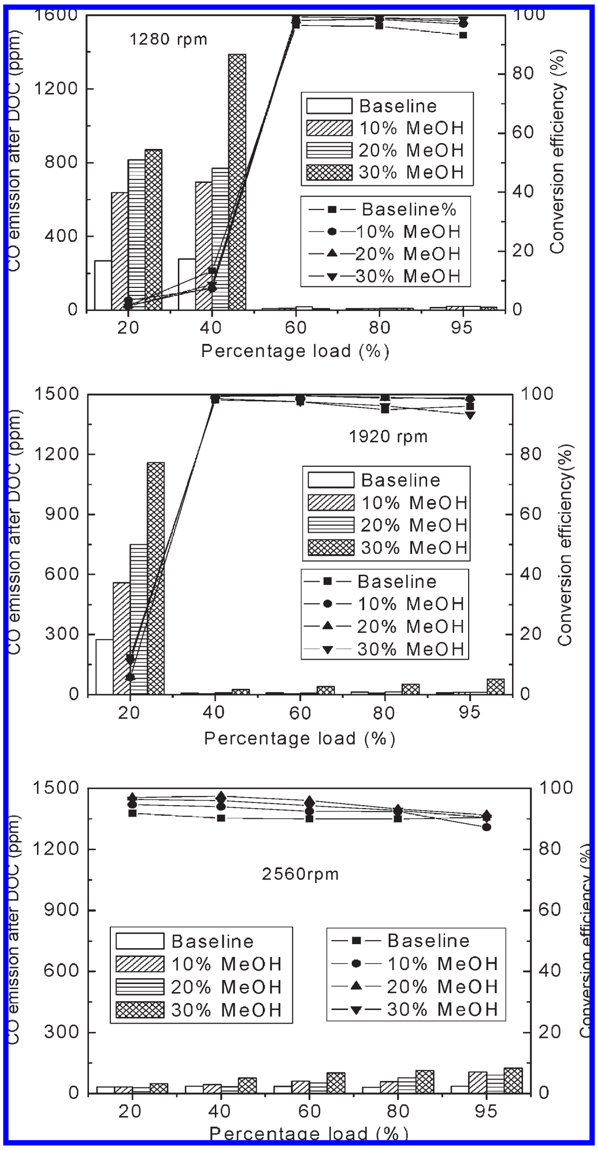

Figure 11. CO emission and conversion efficiency after DOC.

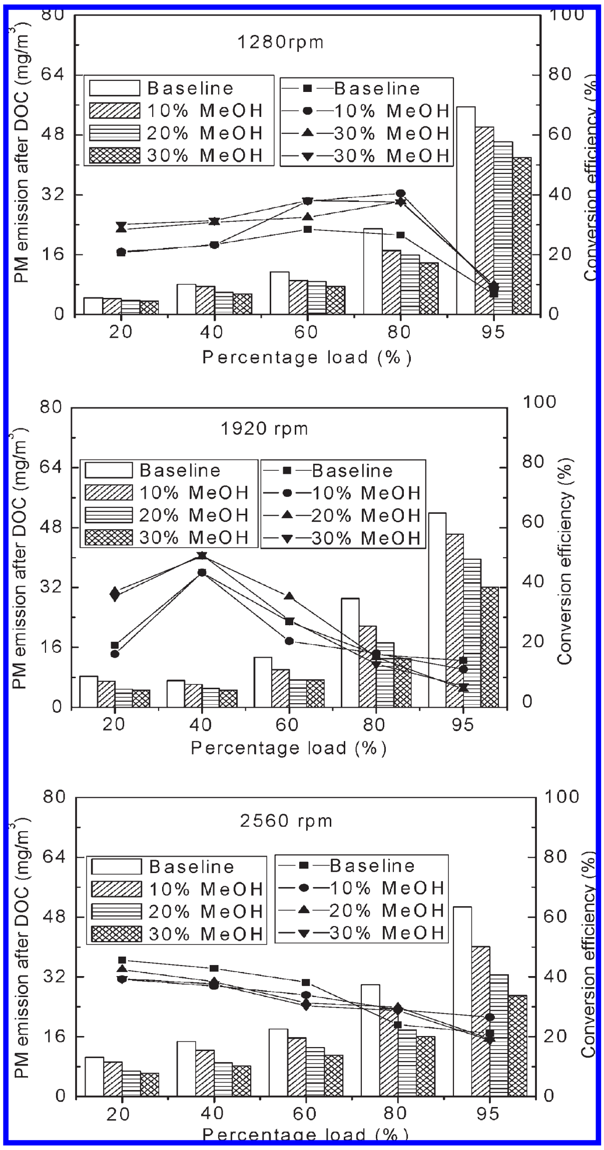

Figure 12. PM emission and conversion efficiency after DOC.

speeds of 1280, 1920, and 2560 rpm, being higher at higher level of fumigation methanol. Kim and Foster[23] also found an increase of formaldehyde with increasing engine loads but little change with engine speed; however, Chao et al.[25] also found high formaldehyde emission from a diesel engine operating on diesel−methanol−ethanol blends.

Formaldehyde is an intermediate combustion product. It begins to form during the process of unburned fuel oxidation after flame propagation.[23] The increase of fumigation methanol leads to a reduction in combustion temperature that might enhance the formation of the intermediate combustion products, including formaldehyde. At low engine load, the combustion temperature is relatively low, and secondary burn-up of unburned fuel is negligible, resulting in high unburned methanol emission but low formaldehyde emission. With an increase in the engine load, the increased combustion temperature promotes the secondary burn-up, and part of the unburned methanol might have been converted into formaldehyde, leading to an increase in formaldehyde and a reduction of unburned methanol in the exhaust gas.

3.4. Effect of Diesel Oxidation Catalyst on the Pollutants. The higher HC, CO, unburned methanol, and formaldehyde emissions are a disadvantage of using the diesel engine with fumigation methanol. In this study, a diesel oxidation catalyst (DOC) was applied to investigate its effectiveness in reducing these emissions.

Figures 10 and 11 show, respectively, the HC and CO emissions after the DOC and their conversion efficiencies. At 20 and 40% engine loads of 1280 rpm, and 20% engine load of 1920 rpm, the HC and CO emissions after the DOC are still high, indicating that the catalytic conversion efficiencies are low. However, at other engine operating conditions, about 80% of HC and over 90% of CO emissions are eliminated by the DOC. As shown in Table 5, the exhaust gas temperatures are below 220 °C at 20 and 40% engine loads of 1280 rpm, and at 20% engine load of 1920 rpm, which is too low for effective oxidation of CO and HC. At the other operating conditions, the DOC can effectively reduce the HC and CO emissions due to sufficiently higher

(25) Chao, H. R.; Lin, T. C.; Chao, M. R.; Chang, F. H.; Huang, C. I.; Chen, C. B. *J Hazard Mater*. **2000**, *B73*, 39–54.

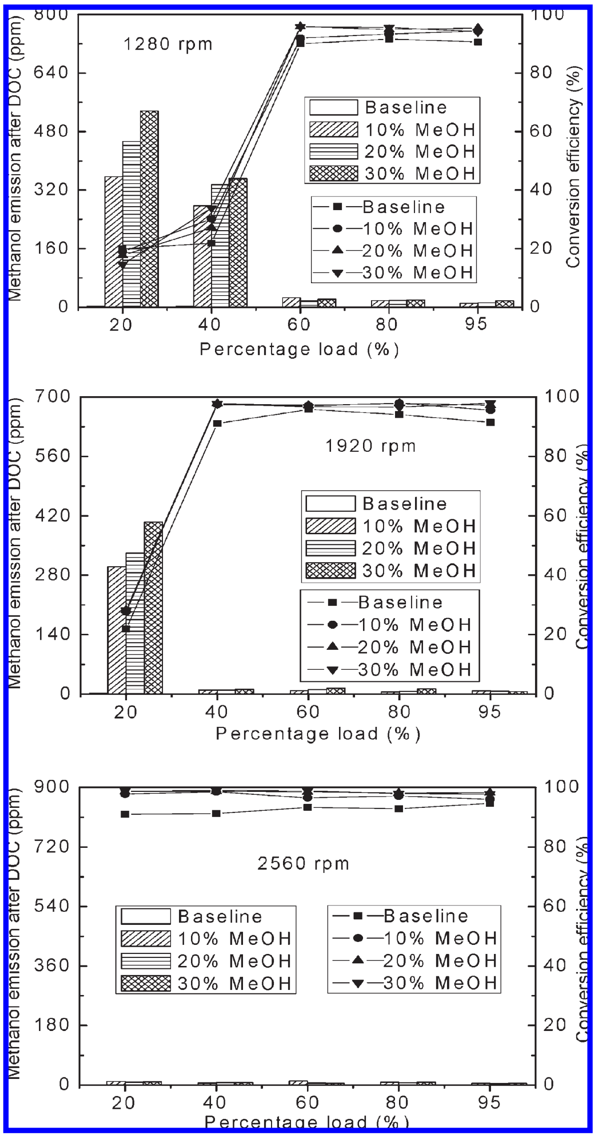

Figure 13. Methanol emission and conversion efficiency after DOC.

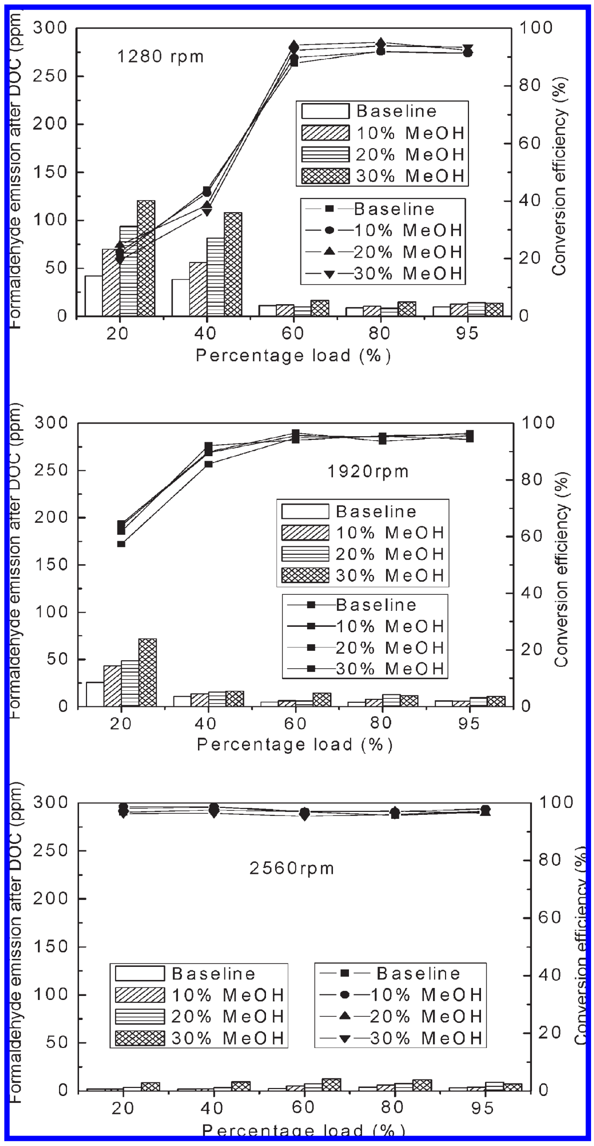

Figure 14. Formaldehyde emission and conversion efficiency after DOC.

exhaust gas temperature. Rideout et al.[26] found that with the DOC, HC, and CO emissions from alcohol-fuelled engines were lower than those from a diesel engine. Yao et al.[13] also found an increase in HC and CO emissions with fumigation methanol, but the DOC could reduce them substantially.

Figure 12 shows the effect of DOC on PM emission. The DOC results in 6.7−38.7, 6.1−51, and 21.2−45.6% reduction in particulate emissions, under different engine loads and fumigation level, for the engine speeds of 1280, 1920, and 2560 rpm, respectively. Pataky et al.[27] have investigated the effect of an oxidation catalytic converter (OCC) on regulated and unregulated diesel emissions. They found that the OCC could reduce PM emissions by 27−54% with the engine operated at three steady state modes, which is in line with the general trend of this study.

It has been shown that methanol applied in the diesel engine can increase the SOF in the particulate[28] and the DOC can effectively reduce the particulate emission due to the oxidation of the SOF.[27,29,30] The same reason might have led to the reduction in PM emission in this investigation.

The effects of the DOC on unburned methanol and formaldehyde emissions, as shown in Figure 13 and 14, are similar to those on HC and CO emissions. At sufficiently high exhaust gas temperature, almost all the unburned methanol and formaldehyde are eliminated. Lipari and Foster[23] suggested that catalytic after-treatment can be a valuable control strategy for HC, unburned fuel, and aldehydes. The results in Sakamoto et al.[31] indicate that over 90% of unburned methanol and formaldehyde are reduced

(26) Rideout, G.; Kirschenblatt, M.; Prakash, C. Emissions from methanol, ethanol, and diesel powered urban transit buses. *SAE Paper 942261*, 1994.
(27) Pataky, G. M.; Baumgard, K. J.; Gratz, L. D.; Bagley, S. T.; Leddy, D. G.; Johoson, J. H. Effects of an oxidation catalytic converter on regulated and unregulated diesel emissions. *SAE Paper 940243*, 1994.
(28) Lin, T. C.; Chao, M. R. *Sci. Total Environ.* **2002**, *284*, 61–74.
(29) Hosoya, M.; Shimoda, M. *Appl Catal.* **1996**, *B10*, 83–97.
(30) Vaaraslahti, k.; Ristimaki, J.; Virtanen, A.; Keskinen, J.; Giechaskiel, B.; Solla, A. *Environ. Sci. Technol.* **2006**, *40*, 4776–4781.
(31) Sakamoto, T.; Sato, Y.; Noda, A. Yamamoto, T. Reduction of unburnt methanol and formaldehyde emissions from methanol fueled vehicles-acceleration of oxidative reduction on catalyst by per-catalyst installation and its heating. *SAE Paper 960238*, 1996.

by the catalyst when the temperature of the catalyst is sufficiently high. The results in Cheung et al.[32] also show 100% reduction in formaldehyde with the DOC for a diesel engine operating on diesel–ethanol blends.

A comparison of the results shows that when the exhaust gas temperature is high enough for lighting-off the DOC, the HC, CO, unburned methanol, and formaldehyde emissions after the DOC are lower than the corresponding emissions from the diesel engine operating on diesel fuel but without the DOC. Thus, the disadvantages of increased HC, CO, unburned methanol, and formaldehyde arising from the use of fumigation methanol can be eliminated with the DOC.

4. Conclusions

Experiments were conducted on a four-cylinder direct-injection diesel engine operating on Euro V diesel fuel and fumigation methanol under different engine loads and engine speeds. A diesel oxidation catalyst was equipped for the purpose of further reducing the pollutants. The following conclusions can be drawn from this study.

(1) When fumigation methanol is applied to the diesel engine, there is a decrease in brake thermal efficiency at low engine loads, but there are no significant changes at medium to high engine loads. The brake thermal efficiency also decreases with engine speed.

(2) Fumigation methanol has the potential for reducing NO_x and particulates emissions in the whole range of engine operation, but it could lead to a significant increase in HC and CO emissions, as well as NO_2 emission. Similar results are obtained at each engine speed.

(3) The application of fumigation methanol shows potential greenhouse benefits at high engine loads with high level of fumigation methanol.

(4) There is a significant increase in unburned methanol and formaldehyde emissions with increase in fumigation level. The methanol emission decreases with increase of engine load whereas the formaldehyde emission increases with engine load. Similar results are obtained at each engine speed.

(5) When the exhaust gas temperature is sufficiently high, the diesel oxidation catalyst can effectively reduce HC, CO, methanol, and formaldehyde emissions, indicating that the DOC is a valuable control strategy for reducing emissions arising from the fumigation methanol. The DOC also leads to further reduction of the PM due to the oxidation of the SOF in the particulate. The effect of the DOC is more prominent at the higher engine speed.

Acknowledgment. The authors wish to thank The Hong Kong Polytechnic University and the Research Grants Council of the Hong Kong SAR (Project No. PolyU 5139/07E) and a research grant from the National Science Foundation Committee of China (contract No. 50876075) for financial support.

(32) Cheung, C. S.; Di, Y. G.; Huang, Z. H. *Atmos. Environ.* **2008**, *42*, 8843–8851.