Effect of diesel detergent synergists on VOCs emissions from engine

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Abstract. In this study, the volatile organic compounds (VOCs) emissions from engine fueled diesel with and without detergent synergist were measured by gas chromatography mass spectrometry(GC-MS). The test results show that compared with reference diesel fuel (without diesel detergent synergist), the use of different diesel detergent synergists has different effects on the VOCs emissions while without after-treatment device. Whether with or without after-treatment device, alkanes always account for the highest proportion of VOCs emissions while engine fuels with different diesel detergent synergists. After-treatment device diesel oxidation catalyst coupled with diesel particulate filter (DOC+DPF) has high catalytic efficiency for VOCs emissions from engine fueled with different fuels, and most of the catalytic efficiency could reach more than 95%.With the catalytic treatment of after-treatment device,the concentrations of carcinogens (detected in this study) in VOCs emissions from engine fueled with and without detergent synergist are far lower than that specified in reference standard GBZ 2.1-2007 “Occupational Exposure Limits for Hazardous Factors in the Workplace and Chemical Hazardous Factors”, respectively. The test results indicate that the use of diesel detergent synergist will not have an adverse impact on human health and it can be safely used.

1 Introduction

With the proposal of China's pledge to be carbon peak by 2030 and carbon neutral by 2060, the problem of vehicle emission control with increasing vehicle ownership has become serious increasingly. Fuel quality has a significant impact on vehicle emissions. The use of fuel additives is one of the effective ways to further improve the fuel quality, and it’s also one of the important measures with wide application and good environmental and economic benefits in the prevention and control of vehicle emission pollutants. In June 2018, the Notice on the Three-year Action Plan to Fight Air Pollution issued by the State Council of China clearly put forward the requirement of "Research the addition of fuel

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detergent synergist meeting environmental protection requirements to vehicle gasoline and diesel fuel before sales" [1]. In January 2021, in the Promotion Catalogue of Green Technology (2020) issued by China's National Development and Reform Commission, "Vehicle fuel detergent synergist technology based on the purpose of combustion and lubrication performance improvement" ranked first [2]. Different from fuel detergent, fuel detergent synergist not only contains polyether amine, polyisobutylene amine and other detergent components, but also adds nitrate compounds, organic peroxides and dinitro compounds that can improve the combustion process, or fatty acids, fatty alcohols and fatty amines that can reduce friction, so as to achieve energy-saving and emission reduction of vehicle. Previously, China's fuel additive regulations only limited its detergency. With the release of various energy-saving and environmental protection policies on fuel detergent synergists, Chinese experts and scholars have also started the evaluation method research on the energy-saving and emission reduction effects of fuel detergent synergists. For example, China’s Shandong Province issued the local standard DB37/T 3862-2020 “Technical Requirements of Gasoline Detergent Synergist” in 2020,which limited the fuel saving effects, emission reduction effects and power improvement effects of gasoline detergent synergist [3]. Before the popularization and application of fuel detergent synergist, it is also necessary to study its impact on environment and human health.

VOCs are important participants in atmospheric chemical processes. Most VOCs have atmospheric chemical reaction activity and are important precursors for the formation of photochemical smoke pollution [4]. Meanwhile, VOCs are important precursors for the formation of ozone in the atmospheric troposphere, and have an important impact on the formation of fine particles and secondary pollution in haze weather, which have attracted more and more attention [5-7]. Foreign countries’ studies on VOCs were earlier. Since the photochemical smog event in Los Angeles, USA in the 1940s, Japan, Britain, Australia, Germany and other developed countries have carried out a large number of studies on VOCs' pollution level and characteristics, composition distribution, source, influencing factors, transfer and transformation [8]. However, the earlier research on VOCs at home and abroad was mainly focused on the atmospheric environment, and the research on vehicle emission sources has gradually increased in recent years [9-12]. In order to explore whether the use of diesel detergent synergist will increase the VOCs emissions that can endanger human health and damage the environment, the VOCs emissions from diesel engine fueled with fuels containing different detergent synergists were compared and analyzed in this study.

2 Experiment setup and procedure

2.1 Fuel and test equipment

2.1.1 Test fuel and diesel detergent synergist

The main physical and chemical properties of the reference fuel used in the test are shown in Table 1. Table 2 shows the additive proportions of diesel detergent synergist samples, which are recommended by the manufacturer. As we can see from Table 2, the recommended additive proportions of different detergent synergist are quite different. The composition of diesel detergent synergists used in the test are confidential. Therefore, it’s unable to analyze the impact of the composition of diesel detergent synergists on VOCs emissions in this study.

Table 1. The main properties of the reference fuel.

Property	Parameters
Density at 20℃ /kg·m^{-3}	825.5
Sulfur content /ppm wt	4.4
PAHs content /wt%	1.4
Cetane index	46
Cetane number	55.7
Freezing point /℃	-13
Cold filter point /℃	-7
Flash point /℃	72

Table 2. Additive proportions of test diesel detergent synergist samples.

Diesel detergent synergist sample	Additive proportion	Diesel detergent synergist sample	Additive proportion
D1	1000 ppmw	D5	2860 ppmv
D2	5000 ppmv	D6	4500 ppmv
D3	9100 ppmv	D7	2860 ppmv
D4	4600 ppmv	D8	4500 ppmv

2.1.2 Test engine and equipment

The test was carried out on a 2.0L diesel engine meeting China V emission standard. The engine is equipped with advanced technologies such as variable geometry turbocharger, high pressure common rail system and dual overhead camshaft hydraulic tappet. The main technical parameters of the engine are shown in Table 3. Summa canister was used to collect exhaust gas in the test, and GC-MS was used to analyze VOCs components. The schematic diagram of engine bench is shown in Fig. 1.

Table 3. Main technical specifications of the diesel engine.

Engine type	4Cylinder, inline, turbocharged, inter-coolingdiesel engine
Bore × stroke /mm×mm	83×92.4
Compression ratio	16.5
Displacement / L	1.999
Rated power @ speed /kW@ r·min^{-1}	105 @ 3600
Max. Torque @ speed /N·m@ r·min^{-1}	320 @ 1600-2600
Rated fuel consumption rate /g·kWh^{-1}	240

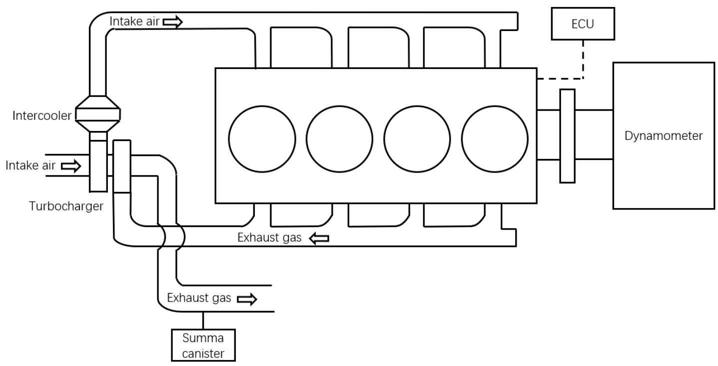

Fig. 1. Schematic of experimental setup.

2.1.3 Emission analysis of VOCs

1)Analytical method

The atmospheric preconcentration system, Agilent 7890b gas chromatograph and Agilent 5977b single quadrupole mass spectrometer were used to detect the VOCs emission concentration from engine fueled with and without the addition of detergent synergist in diesel fuel. The instrument system is equipped with Dean switch central cutting device, cold column oven and FID. The exhaust samples collected in summa canisterare preconcentrated by cold trap to remove water and inert gas, and then are injected into gas chromatograph for separation. C2 and C3 compounds are analyzed by HP plot Q column and FID channel, and other compounds are analyzed by DB-1 column and MSD channel.

2)Standard gases

The standard gases used in the test were 57 PAMS ozone precursor standard gases (1 μmol/mol, 1L), 65 TO-15 standard gases (1 μmol/mol) and 13 aldehydes and ketones, all of which were purchased from Linde Company. There are 14 compounds overlapping in PAMS standard gases and TO-15 standard gases, and 3 compounds (acrolein, acetone and 2-butanone) overlapping in 13 aldehydes and ketones and TO-15 standard gases. Therefore, 108 compounds could be measured quantitatively by this method.

2.2 Engine bench test method

The VOCs emission test condition was WHSC cycle according to GB 17691-2018 "Limits of Measurement Methods for Emissions from Diesel Fuelled Heavy-duty Vehicles (CHINA VI)" [13]. The VOCs emissions of the engine fueled with reference diesel fuel and the reference diesel fuel containing different detergent synergists were detected. Meanwhile, in order to explore the influence of after-treatment device on VOCs emissions, the VOCs emissions with and without DOC+DPF were tested.

During the test, a3.2L summa canister was used to collect gaseous pollutants in WHSC cycle. Before collection, the summa canister was cleaned by canister clean device. After cleaning, the summa canister was pumped to vacuum (<10 Pa) and ready for use. After installing the particulate filter and flow controller, opened the valve of the sampling canister to start constant current sampling of gaseous pollutants during WHSC cycle. The collection time was 1895 s and the collection flow was 101.3 mL/min. After the set sampling time arrived, closed the valve and sealed it with a sealing cap.

3 Results and discussion

3.1 Emissions of different kinds of VOCs

3.1.1 Emissions of different kinds of VOCs without after-treatment device

Fig. 2 shows the emissions of different kinds of VOCs without after-treatment device when the engine uses different diesel detergent synergists. It can be seen from Fig. 2 that compared with the reference diesel fuel, the total VOCs emissions of the engine using D1, D2, D6 and D8 diesel detergent synergists are reduced, and the use of other detergent synergists causes a small increase in VOCs emissions while without after-treatment device. Among the VOCs emissions without after-treatment, the proportion of alkanes is the highest. The proportion of alkanes in the VOCs emissions when engine fuels with different fuels is almost higher than 50%, followed by aromatic hydrocarbons, aldehydes and ketones, while the proportion of halogenated hydrocarbons in VOCs is small. The research of Qin et al. showed that the proportion of alkanes in VOCs emissions of GDI and PFI gasoline engine exhaust was quite high, reaching 39%-51% [5].

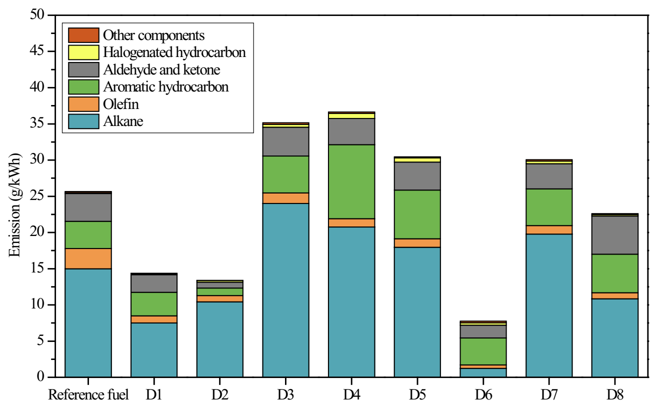

Fig. 2. Emissions of different kinds of VOCs without after-treatment device.

3.1.2 Emissions of different kinds of VOCs with after-treatment device

After-treatment device DOC+DPF has high catalytic efficiency for VOCs emissions from engine fueled with diesel containing different detergent synergists. After the catalytic treatment of DOC+DPF, the VOCs emissions are almost reduced by about 95%.When fueling with reference diesel, aldehydes and ketones account for the highest proportion of VOCs emissions with after-treatment, followed by aromatic hydrocarbons. After using different diesel detergent synergists, alkanes still account for the highest proportion of VOCs emissions with after-treatment, followed by halogenated hydrocarbons. The proportion of aldehydes, ketones and aromatic hydrocarbons in VOCs is significantly reduced, indicating that DOC+DPF has high catalytic efficiency on these compounds. In general, the use of diesel detergent synergist leads to a small increase in VOCs emissions with after-treatment device, and the proportion of alkanes is the highest.

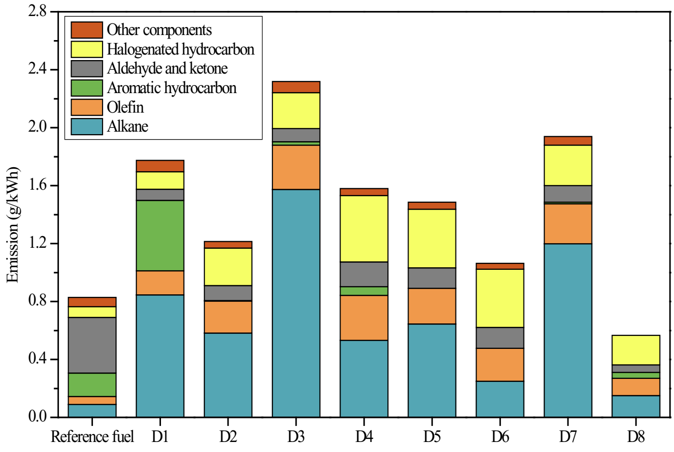

Fig. 3. Emissions of different kinds of VOCs with after-treatment device.

3.2 Emissions of VOCs components which have larger hazards to human health

According to the list of carcinogens of the International Agency for Research on Cancer of the World Health Organization, VOCs components with larger hazards to human health in this study were screened, as shown in Table 4. Among them, grade 1 carcinogens are determined to be carcinogens to human beings. Three grade 1 carcinogens including 1,3-butadiene, benzene and 1,2-dichloropropane were detected in the test. Grade 2B carcinogens are substances that may cause cancer to humans. Six kinds of grade 2B carcinogens were detected in the test, namely acetaldehyde, chloroform, 1,2-dichloroethane, carbon tetrachloride, ethylbenzene and naphthalene. 1,3-butadiene has anesthetic and stimulating effects, and it can cause acute poisoning and chronic effects, and has certain toxic effects on occupational exposed people, and pollutes water, soil and atmosphere [14, 15]. A large part of leukemia patients have a history of exposure to benzene and its organic products. Long term inhalation of benzene will damage people's nervous system, and acute poisoning will produce nerve spasm, coma and even death [16, 17]. 1,2-dichloropropane has inhibitory effect on human central nervous system and mild irritation to skin and eyes [18]. Since there is no international standard for VOCs emissions from vehicle exhaust, the allowable concentrations of unconventional pollutants in GBZ 2.1-2007 “Occupational Exposure Limits for Hazardous Agents in the Workplace Chemical Hazardous Agents” are given as a reference, including the maximum allowable concentration, time weighted average allowable concentration and short-term exposure allowable concentration [19]. Since the average concentration of pollutants in WHSC cycle is analyzed in this study, the time weighted average allowable concentration in Table 4 is mainly used as the reference concentration value for pollutant emission evaluation before and after the use of detergent synergist in the following analysis. Because the time weighted average allowable concentration of acetaldehyde is not specified in the standard, the maximum allowable concentration is used as the reference concentration for acetaldehyde emission evaluation.

Table 4. VOCs components which have larger hazards to human health in this study.

Number	Component	Carcinogenic grade	GBZ 2.1-2007 "Occupational Exposure Limits for Hazardous Agents in the Workplace Chemical Hazardous Agents"		
			Maximum allowable concentration /mg·m^{-3}	Time weighted average allowable concentration /mg·m^{-3}	Short-time exposure allowable concentration /mg·m^{-3}
1	1,3-butadiene	Grade 1	—	5	—
2	Benzene	Grade 1	—	6	10
3	1,2-dichloropropane	Grade 1	—	350	500
4	Acetaldehyde	Grade 2B	45	—	—
5	Chloroform	Grade 2B	—	20	—
6	1,2-dichloroethane	Grade 2B	—	7	15
7	Carbon tetrachloride	Grade 2B	—	15	25
8	Ethylbenzene	Grade 2B	—	100	150
9	Naphthalene	Grade 2B	—	50	75

3.2.1 1,3-butadiene, benzene and 1,2-dichloropropane emissions

The emissions of three grade 1 carcinogens, 1,3-butadiene, benzene and 1,2-dichloropropane from engine fueled with reference diesel and reference diesel containing different diesel detergent synergists are shown in Fig. 4 - Fig.6. The values in brackets in the caption of the figure are the time average weighted allowable concentration or maximum allowable concentration in GBZ 2.1-2007, which are used as a reference, the same below.

The research of Takada et al. shows that the1,3-butadiene in enigne exhaust is mainly formed under the conditions of high exhaust temperature and oxygen enrichment, and it is very easy to decompose in a short time [20]. It can be seen from Fig. 4 that there are less 1,3-butadiene emissions before and after the use of diesel detergent synergists, and none of them exceeds the time weighted average allowable concentration in GBZ 2.1-2007. Except for D1 diesel detergent synergist, the use of other diesel detergent synergists can reduce the 1,3-butadieneemissions while without after-treatment device, and the 1,3-butadiene emission of using D6 diesel detergent synergist is almost zero. After the catalytic treatment of DOC+DPF, almost no 1,3-butadiene could be detected in the VOCs emissions from engine. Therefore, compared with the combustion of reference diesel, the use of diesel detergent synergist does not increase the emissions of 1,3-butadiene.

The main source of benzene in engine exhaust is formed by pre-synthesis and structural reorganization of incomplete combustion fuel molecules during combustion [21]. Fig. 5 shows the benzene emissions before and after the engine uses diesel detergent synergist. It can be seen from Fig. 5 that except for D1 and D2 diesel detergent synergists, the use of other diesel detergent synergists increases the benzene emissions while without after-treatment device, and the emissions increase to 50% - 180% compared with that of reference diesel. However, after the catalytic treatment of the after-treatment device, the benzene emissions in exhaust gas are almost completely eliminated. The research by Misawa et al. also shows that after-treatment device has high catalytic efficiency on the benzene emissions of diesel engine [22]. The benzene emissions before and after the use of diesel detergent synergist without after-treatment device significantly exceed the time weighted average allowable concentration in GBZ 2.1-2007, but after the catalytic treatment of DOC+DPF, the benzene emissions are all lower than the average allowable concentration.

There are few reports on the test of 1,2-dichloropropane emissions from engine at home and abroad. The test results of this study indicate that the emissions of 1,2-dichloropropane in diesel engine exhaust can not be ignored. The 1,2-dichloropropane emissions before and after the engine uses diesel detergent synergist are shown in Fig. 6. It can be seen from Fig. 6 that except for D1 diesel detergent synergist, the use of other diesel detergent synergists leads to an increase in the emissions of 1,2-dichloropropane under the conditions of with and without after-treatment device. Compared with reference diesel, the use of D4 diesel detergent synergist results in the highest increase in 1,2-dichloropropane emission while without after-treatment device. When the engine fuels with diesel containing D4 detergent synergist, the 1,2-dichloropropane emissions with and without after-treatment device are 142.6 mg/m^3 and 74.9 mg/m^3 respectively, which are 5.5 times and 3.9 times higher than that of reference diesel. After the catalytic treatment of DOC+DPF, the 1,2-dichloropropane emissions when the engine fuels with diesel containing D3, D4, D5, D7 detergent synergists can be reduced by 50%. The emission concentrations of 1,2-dichloropropane from engine fueled with different fuels do not exceed the time weighted average allowable concentration value in GBZ 2.1-2007.

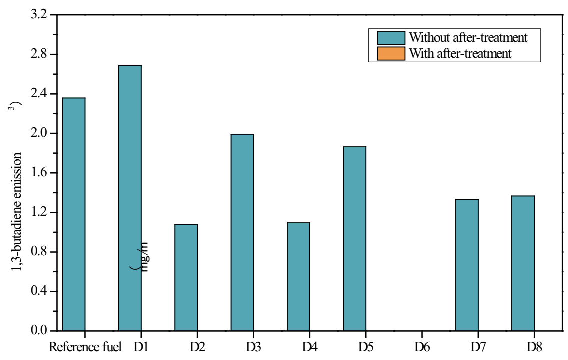

Fig. 4. 1,3-butadiene emissions from engine fueled with different fuels (The average allowable concentration is 5 mg/m^3)

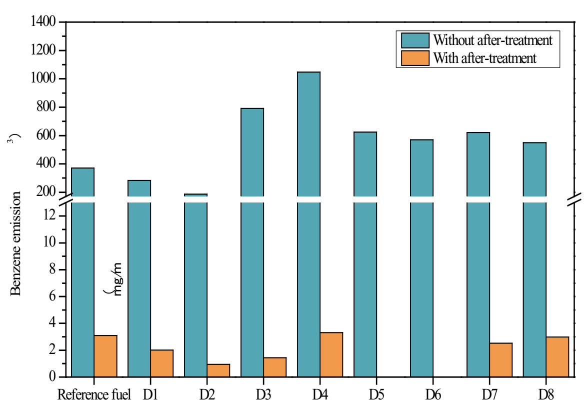

Fig. 5. Benzene emissions from engine fueled with different fuels (The average allowable concentration is 6 mg/m^3).

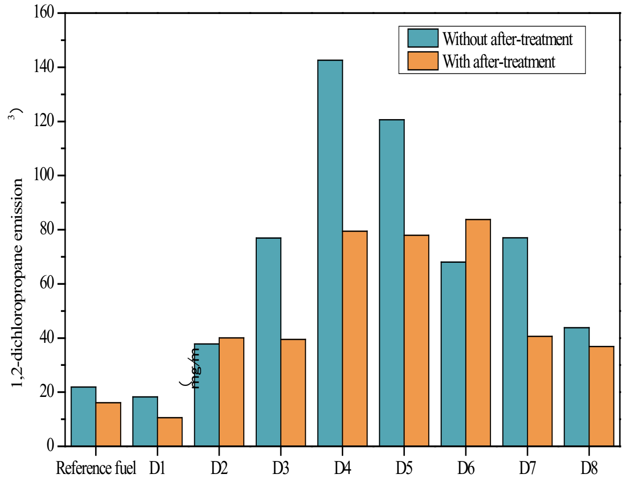

Fig. 6. 1,2-dichloropropane emissions from engine fueled with different fuels (The average allowable concentration is 350 mg/m^3)

3.2.2 Acetaldehyde and chloroform emissions

The acetaldehyde emission in engine exhaust mainly comes from the incomplete combustion of alcohol fuel, so the research about it focuses mainly on the engine fueled with alcohol alternative fuels such as ethanol and methanol [23-25]. The test results of this study show that a small amount of acetaldehyde also could be generated in the combustion of diesel fuel. Fig. 7 shows the acetaldehyde emissions before and after the engine uses diesel detergent synergist. The acetaldehyde emissions of the engine using D1, D2 and D6 detergent synergists are lower than that of fueling reference diesel, and the acetaldehyde emissions after using other diesel detergent synergists are not different from that of reference diesel under without after-treatment device condition. After the catalytic treatment of after-treatment device, the acetaldehyde emissions of the engine after using detergent synergists are lower than that of fueling reference diesel, and none of them exceeds the time weighted average allowable concentration value in GBZ 2.1-2007.

Fig.8 shows the emissions of chloroform before and after the engine uses diesel detergent synergist. It can be seen from Fig. 8 that the combustion of reference diesel almost no chloroform is emitted. Except for D8 diesel detergent synergist, the use of other diesel detergent synergists produces chloroform emissions while with or without after-treatment device. However, the chloroform emissions are quite less, most of which is about 0.6 mg/m^3, which is far lower than the time weighted average allowable concentration (20 mg/m^3) in GBZ 2.1-2007.

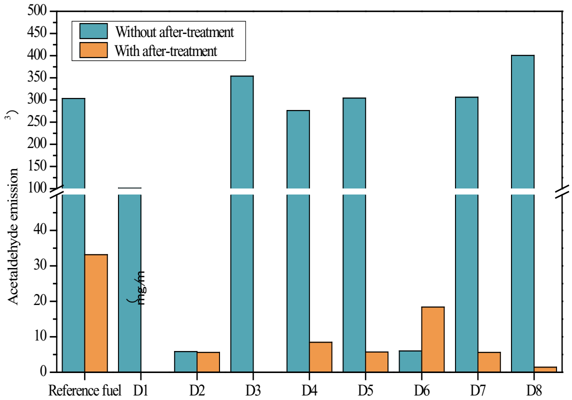

Fig. 7. Acetaldehyde emissions from engine fueled with different fuels (The average allowable concentration is 45 mg/m^3).

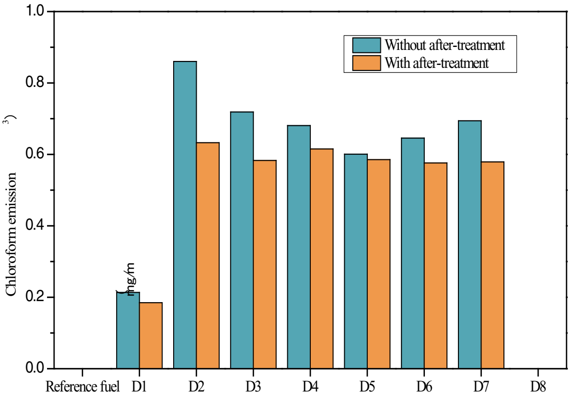

Fig. 8. Chloroform emissions from engine fueled with different fuels (The average allowable concentration is 20 mg/m^3).

3.2.3 1,2-dichloroethane and carbon tetrachloride emissions

Fig. 9 shows the emissions of 1,2-dichloroethane before and after the engine uses diesel detergent synergist. The emissions of 1,2-dichloroethane after using D8 diesel detergent synergist are almost the same as that when only fueling with reference diesel. The use of other detergent synergists produces a small amount of 1,2-dichloroethane emissions, and the maximum emission is only 1.13 mg/m^3. After the catalytic treatment of DOC+DPF, the 1,2-dichloroethane emissions from the engine using different detergent synergists are basically eliminated, and the emission concentration is far lower than the time weighted average allowable concentration (7 mg/m^3) in GBZ 2.1-2007.

Fig. 10 shows the emissions of carbon tetrachloride before and after the engine uses diesel detergent synergist. Engine fueling reference diesel causes carbon tetrachloride emissions of about 2.5 mg/m^3. The use of D8 diesel detergent synergist increases the carbon tetrachloride emission while without after-treatment device, and the use of other detergent synergists does not produce carbon tetrachloride emissions.

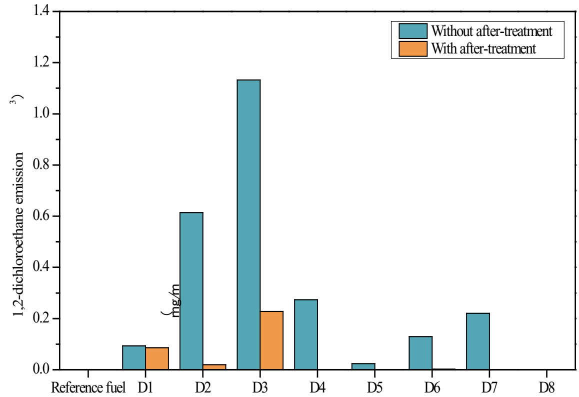

Fig.9. 1,2-dichloroethane emissions from engine fueled with different fuels (The average allowable concentration is 7 mg/m^3)

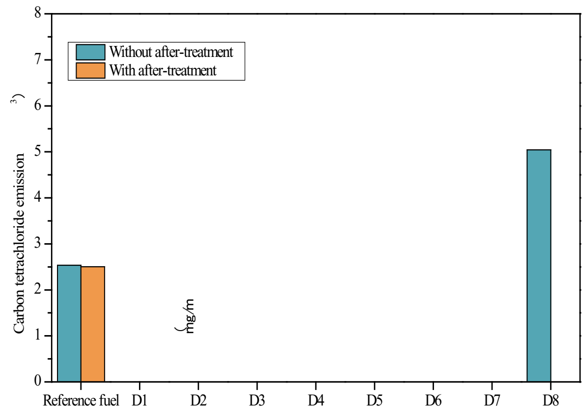

Fig.10. Carbon tetrachloride emissions from engine fueled with different fuels (The average allowable concentration is 15 mg/m^3)

3.2.4 Ethylbenzene and naphthalene emissions

The ethylbenzene emissions of the engine after using diesel detergent synergist are lower than that of reference diesel. The ethylbenzene emission of the engine after using D5 diesel detergent synergist is almost zero, as shown in Fig. 11. Similarly, the ethylbenzene emissions caused by the use of different diesel detergent synergists are far lower than the time weighted average allowable concentration in GBZ 2.1-2007.

As shown in Fig. 12, the use of D4, D5, D7 and D8 diesel detergent synergists increases the naphthalene emissions while without after-treatment device. The naphthalene emission after using D4 diesel detergent synergist are the highest, which can reach 629 mg/m^3. However, the catalytic effect of DOC+DPF on naphthalene is obvious. After the catalytic treatment of DOC+DPF, the naphthalene emissions of the engine fueling different fuels are almost zero. Only the use of D1 diesel detergent synergist slightly increases the naphthalene emission while with after-treatment device, which is 22.3mg/m^3, but the concentration does not exceed the time weighted average allowable concentration in GBZ 2.1-2007. After the engine exhaust diffuses into the air, the pollutant emission concentration will be diluted, so the concentration will not have an adverse impact on human health.

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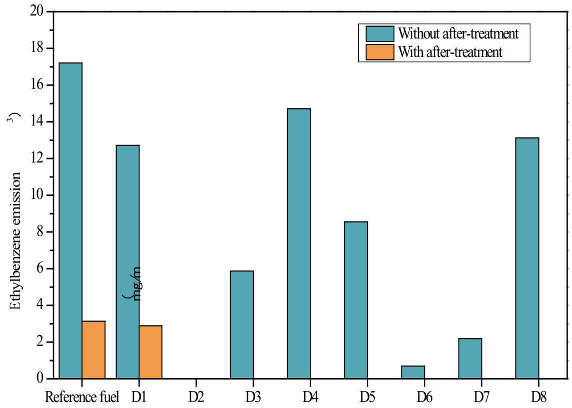

Fig. 11. Ethylbenzene emissions from engine fueled with different fuels
(The average allowable concentration is 100 mg/m^3).

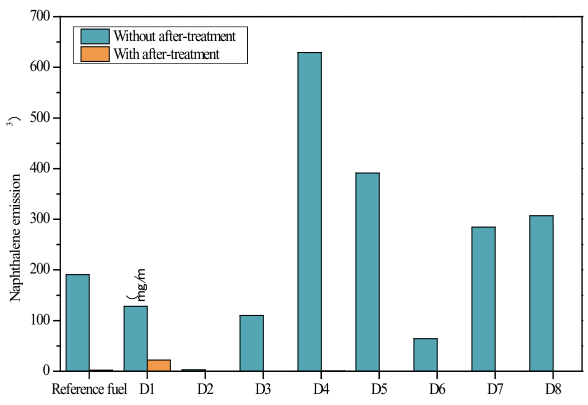

Fig.12. Naphthalene emissions from engine fueled with different fuels
(The average allowable concentration is 50 mg/m^3)

4 Conclusions

In this study, GC-MS was used to detect the VOCs emissions of diesel engine before and after using eight commercially available diesel detergent synergists, and the emissions of pollutants harmful to human health were analyzed. The conclusions of this study are drawn as follows :

1) Some of the diesel detergent synergists leads to a decrease of VOCs emissions while without after-treatment device, but the others are just the opposite. DOC+DPF has high catalytic efficiency for VOCs emissions from engines fueled with different fuels, and most of the catalytic efficiency can reach more than 95%. Whether with or without after-treatment, alkanes always account for the highest proportion of VOCs emissions from engines using different diesel detergent synergists.

2) The same as the effect on VOCs emisisons, some of the diesel detergent synergists leads to a decrease in the emissions of some grade 1 carcinogens and grade 2B carcinogens, but the others are just the opposite. After the catalytic treatment of the after-treatment device, the emissions of all carcinogens detected in this study are far lower than the time

weighted average allowable concentration in GBZ 2.1-2007. The use of diesel detergent synergist will not have an adverse impact on human health and it can be safely used.

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