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Analysis of Carbon Particulate Matter Removal Performance of Dual-Fuel Marine Engine with DOC + CDPF

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Abstract: This study analyzes Diesel Oxidation Catalyst (DOC) and Carbon Diesel Particulate Filter (CDPF) after-treatment systems integrated into a WARTSILA W20DF marine dual-fuel engine. The CDPF was coated with a non-precious metal catalyst whose catalytic redox performance improved with increasing temperature. The carbon particulate matter combustion reached up to 12.5 mg/s at 800 K and over 20 mg/s at 900 K. Then, the W20DF running at 230 kW, 450 kW, 680 kW, and 810 kW with 1000 rpm; a Tisch 10-8xx; and an AVL SPC 478 were used to sample and analyze the carbon particulate matter (CPM) before and after DOC + CDPF. The gaseous emissions (O_2, CO_2, CO, HC, NOx, and NO_2) were analyzed with the flue gas analyzer AVL i60. The results show that the collected carbon particulate matter simultaneously became darker as the load decreased. This study finds that the maximum amount of CPM per unit volume of exhaust gas occurs under 50% working conditions and the lowest amount under 90% working conditions. After DOC + CDPF treatment with a non-precious metal coating, the CPM was reduced by about 50%. Furthermore, this type of catalyst's efficiency rises with the temperature increase. The CPM combustion efficiency reached up to 20 mg/s at 900 K. The other gas components in the exhaust gas before and after DOC + CDPF also changed. These research results have a significant reference value for DOC + CDPF optimization to decrease the carbon particulate matter in marine engines.

Keywords: carbon particulate matter; dual fuel; marine engine; DOC + CDPF; emission

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1. Introduction

The development of the marine ship made a great contribution to the prosperity of the ship transportation industry, whereas the emissions from marine engines are a significant source of air pollution [1,2]. As is known, the emission of CO_2 is one major cause of the greenhouse effect [3,4]. The emission of carbon particulate matter (CPM) is another. CPM can be suspended in the atmosphere for a long time, is extremely harmful to the human respiratory and blood circulation systems, easily enters the ship's ventilation pipeline system, and pollutes the living environment of the crew [5,6]. As the main pollutant of ship diesel engines, the problem of CPM purification is receiving more and more attention. Currently, the International Maritime Organization, the United States, the European Union, and China have all established ship emission regulations that set emission limits for CPM [7,8]. Under the environmental protection trend of preventing air pollution from ships, it is necessary to research marine diesel engine CPM emission control technology to cope with the increasingly stringent regulatory requirements [9,10]. The installation of DOC + CDPF is the most effective measure for reducing exhaust CPM and has been the focus of research in recent years [11,12].

Diesel particulate matter emitted by ship engines is a mixture of different kinds of particles with sizes spanning from a few nanometers to several microns. Among them, soot particles are related to severe pathologies and are classified by the World Health

Organization as carcinogens of Class I [13]. Marine diesel engines also contribute to the emission of black carbon, which is recognized as an important climate-forcing agent. In 2015, Francesco Di Natale presented a survey on the state-of-the-art knowledge of the physical–chemical properties, toxicology, and emissions of particles from ships [14]. In 2019, Jiang Hao also investigated the characteristics of the CPM sampled from the exhaust of a low-speed two-stroke common-rail marine diesel engine fueled with HFO at different loads [15]. With the optimization of the combustion technology of marine diesel engines, especially after dual-fuel engines have gradually gained market recognition, there are relatively few studies related to their carbon-containing particulate matter emission performance. This paper focuses on WARTSILA W20DF to sample and analyze its CPM emission characteristics, provide a reference for optimizing technical measures, and reduce CPM emissions from marine engines.

An integrated after-treatment system consisting of DOC and CDPF is an effective way to reduce carbon particulate matter [16,17]. The particle trap technology on the market is more mature and the particulate trap efficiency is high, reaching more than 90% [18–20]. In 2019, Shao Shushan's study showed that the CPM emission characteristics of engineering vehicle diesel engines improved observably under 3 different conditions with DOC + CDPF, and its CPM emission was reduced by over 85% [21]. Wang Deyuan found that significantly increasing the HC concentration can increase the particle oxidation rate, but it has little effect on the overall regeneration rate and increases the HC slip amount [22]. Jie Hu investigated the effect of DOC + CDPF + SCR on NOx and particle emissions during different operations to assess the applicability of this after-treatment for meeting more rigorous non-road emissions standards. The results showed that DOC + CDPF has no significant effect on NOx but increases the NO_2/NOx ratio correlated with load [23]. However, the above studies were conducted on the bench of land-based diesel engines, and there is a lack of corresponding studies regarding the special use scenarios of marine diesel engines.

In summary, the current research on diesel particulate reduction devices is mainly focused on theoretical and simulation aspects. Less research has been conducted in the area of diesel particulate reduction management for marine engines [24–26]. There are even fewer studies related to carbon particulate matter emissions from modern large marine diesel engines and new dual-fuel engines in particular. Therefore, it is of great practical significance to carry out research on marine diesel engine particulate matter emission control technology and form a perfect CPM control technology and device for ocean-going and inland river vessels to meet the challenges of international regulations on marine diesel engine CPM emissions. Therefore, it is necessary to research marine diesel particulate matter control technology, complete the development of CPM control devices, and form a CPM reduction program applicable to many types of marine diesel engines.

In addition, the catalyst is critical to the efficiency of carbon particulate removal from the exhaust gas. In this paper, a performance study of one type of non-precious metal catalyst for carbon removal is carried out. In addition, the particulate emission characteristics of marine engines are studied, focusing on a modern WARTSILA W20DF dual-fuel engine. Finally, a study of the efficiency of carbon particle removal from WARTSILA W20DF exhaust gas by DOC + CDPF coated with this type of catalyst is carried out. The research results have important reference value for decreasing the CPM of marine engines and further promoting the transformation and upgrading of the ship industry to green technology.

2. Test Bench and Method

The experiments were carried out on a pressurized inter-cooled and four-stroke fixed-speed marine dual-fuel engine, the WARTSILA W20DF, with diesel oil. The kinematic viscosity at 20 °C of the diesel used in the experiments was 3.1 mm^2/s, with a density of 833.5 Kg/m^3, a calorific value of 39.2 MJ/kg, and a residual carbon value of 0.21%. The engine has 6 cylinders, and each cylinder liner diameter is 200 mm, its rated work condition being 1000 rpm and 900 kW. The detailed technical parameters of the machine are shown in

Table 1. A DOC + CDPF device was installed in the exhaust pipe to capture and catalytically oxidize the carbon particles in the exhaust gas. The length and width of DOC + CDPF were 528 mm, the lengths of DOC and CDPF were 75 mm and 400 mm, respectively, and its hole distribution density was 200 cpsi. AVL SPC 478 and Tisch 10-8xx (AVL SPC 478: AVL List GmbH, Hans-List-Platz 1, 8020 Graz, Austria; Tisch 10-8xx:145 South Miami Avenue Village of Cleves, Ohio 45002, USA)were used for sampling and analyzing the particulate matter in the exhaust gas before and after the reactor. AVL i60 was also used to analyze the content of O_2, CO_2, CO, HC, NOx, and NO in the exhaust gas. In addition, the pressure difference before and after the reactor was monitored to determine whether the CDPF trap was blocked and to analyze the catalytic oxidation efficiency. The principle of the experimental bench is shown in Figure 1, which is used to analyze the effect of this type of DOC + CDPF device on reducing particulate matter emissions from marine diesel engines.

Table 1. Main technical parameters of the WARTSILA W20DF marine engine.

Technical Parameter	Value
Type of air intake	Pressurized inter-cooled
Number of cylinders	6
Ignition sequence	1-5-3-4-2-6
Rated condition	1000 rpm/900 kW
Stroke/cylinder bore	280 mm/200 mm
Compression ratio	13.3
Injection time	16 °C A before TDC
Air intake timing	13 °C A before TDC/44 °C A after BDC
Exhaust valve timing	39.5 °C A before BDC/12 °C A after BDC

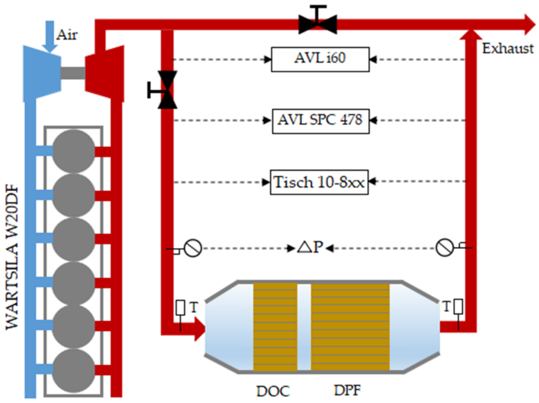

Figure 1. Test bench of the WARTSILA W20DF marine engine.

The AVL SPC 478 collects carbon particles from exhaust gas in a single-stage filtration process. It uses a fluorocarbon-coated glass-fiber filter paper with a diameter of 70 mm and a thickness of 0.178 mm. The collection efficiency for 0.3 µm particles is not lower than 95% when the gas flow rate is between 35 and 80 cm/s. After 20 min of sampling, the change in filter-paper weight was calculated to judge how many carbon particles there were in the exhaust gas. The carbon particles on the filter paper were also observed and analyzed under a high-magnification microscope. The Tisch 10-8xx uses aerodynamic principles similar to those of the human respiratory system to collect particulate matter stage by stage. Numerous small round jets improve collection efficiency and provide a sharper cutoff of particle sizes in each stage of inertial impactors. The Tisch 10-8xx has 8 stages and, with glass-fiber filter paper of different pore sizes, can collect particles with sizes ranging from 0.43 to 10 microns. More detailed parameters of Tisch 10-8xx are shown in Table 2. It uses a vacuum pump to provide exhaust gas at 28.3 L per minute. After 10 min of sampling for each condition, the carbon particulate matter content of the exhaust gas was analyzed by weighing the filter paper.

Table 2. Technical parameters of the Tisch 10-8xx sampler.

Stage	Orifice Diameter (mm)	Number of Holes	Range of Particle Sizes (μm)
1	2.55	96	9.0–10
2	1.89	96	5.8–9.0
3	0.91	400	4.7–5.8
4	0.71	400	3.3–4.7
5	0.53	400	2.1–3.3
6	0.34	400	1.1–2.1
7	0.25	400	0.65–1.1
8	0.25	201	0.43–0.65

The WARTSILA W20DF engine was maintained at 1000 rpm, and carbon particulate matter was collected under 25%, 50%, 75%, and 90% operating conditions. The 4 operating conditions correspond to the powers of 229, 451, 677, and 812 kW, respectively.

3. Principle of DOC + CDPF

The DOC + CDPF device in this experiment uses SiC as the carrier, coated with non-precious metal catalyst, with a pore distribution density of 200 cpsi, the size of the device being 176 × 176 × 400 mm.

As is known, more than 90% of the NOx in the exhaust gas is NO. The DOC converts NO to NO_2, which can promote the oxidation of carbon particulate matter in the DPF. Some CO and HC in the exhaust gas are oxidized to CO_2 and H_2O, respectively, in the DOC. However, the DOC cannot capture the CPM because it is only slightly oxidized. The detailed chemical reactions are depicted as follows [27]:

$$2CO + O_2 \rightarrow 2CO_2$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$4CH + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

The CDPF captures the CPM and oxidizes it to CO or CO_2 in the presence of oxygen and nitrogen dioxide, thus keeping the exhaust gas in the CDPF unobstructed. The detailed chemical reactions are depicted as follows [27]:

$$2C + O_2 \rightarrow 2CO$$

$$2C + O_2 \rightarrow CO_2$$

$$C + NO_2 \rightarrow CO + NO$$

$$C + 2NO_2 \rightarrow CO_2 + 2NO$$

$$2C + 2NO_2 + O_2 \rightarrow 2CO_2 + 2NO$$

$$2C + 2NO_2 + O_2 \rightarrow 2CO + 2NO_2$$

4. Test Results and Analysis

In this paper, the effect of gas temperature and NOx content in gas on catalyst performance was first analyzed in small bench experiments. Later on, focusing on the WARTSILA W20DF marine engine bench, studies were performed concerning the analysis of the percentage of each particle size of the carbon particulate matter in the exhaust gas of the engine, the removal efficiency of the carbon particulate matter, and each gas's composition in the exhaust gas before and after the DOC + CDPF reactor. The specific results are analyzed as follows.

4.1. Catalyst Performance under Different Temperatures

The non-precious metal catalyst was coated on the carrier at 350 g/m^3 to study the catalytic oxidation–reduction performance under different temperature conditions. The relevant results are shown in Figure 2. The catalyst performance was gradually optimized from 473 K to 873 K. However, the catalyst performance was relatively poor at temperatures below 723 K, and the particulate matter combustion rate was only 0–5 mg/s. Only after reaching 723 K did the rate of particulate matter removal increase rapidly, and the combustion rates at 773 K, 823 K, and 873 K were 7.5 mg/s, 16.3 mg/s, and 19.8 mg/s, respectively. Therefore, to increase the reaction rate of particulate combustion, the CDPF inlet flue gas must be maintained at a temperature greater than 773 K. The higher the temperature, the better the effect.

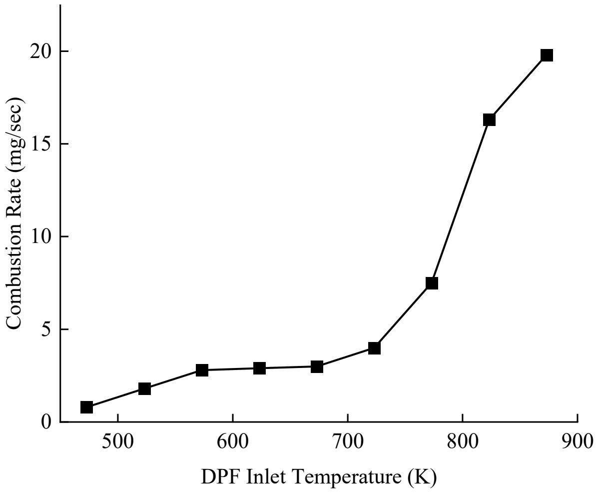

Figure 2. Catalyst performance under different temperatures of CDPF inlet.

4.2. Effect of NOx Concentration

When the soot loading in the exhaust gas is 7 g/L at 823 K and 873 K, the regeneration ratio of particulate combustion by this type of catalyst is greater than 80%. As shown in Figure 3, the CDPF combustion regeneration ratio reached up to 91% with 1500 ppm NOx in the exhaust gas inlet at 873 K. As the NOx concentration decreased to 1350 ppm, the regeneration ratio decreased to 87%, and the regeneration ratio was reduced to 85% when the NOx concentration in the inlet gas was 30 ppm. The same pattern of change can be observed in the regeneration ratio of carbon particulate removal by non-precious metal catalysts at an inlet gas temperature of 823 K. With this type of non-precious metal catalyst, the NOx content in exhaust gas from a diesel engine is favorable for enhancing the particulate combustion efficiency.

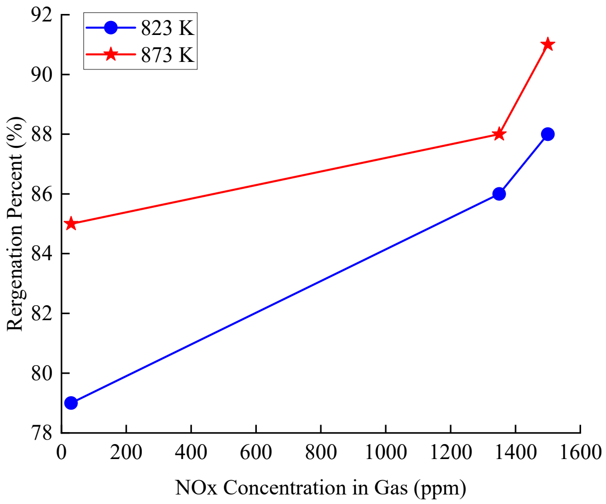

Figure 3. Catalyst performance under different NOx concentrations in the exhaust gas.

4.3. Test Results of WARTSILA W20DF

The WARTSILA W20DF marine engine was maintained at 1000 rpm and was run at 4 operating conditions of 25%, 50%, 75%, and 90%. The power of each operating condition was 230 kW, 450 kW, 680 kW, and 810 kW, respectively, and the gas composition was O_2, CO_2, CO, NO, and NO_2. Particulate matter in the exhaust gas before and after DOC + CDPF was analyzed using AVL i60, AVL SPC 478, and Tisch 10-8xx.

4.3.1. Original Emissions

The raw emission parameter values of the WARTSILA W20DF marine engine are shown in Table 3. NOx emission is about 850 ppm for this kind of marine engine. Emissions of particulate matter CO, HC, and CO_2 were 0.024 mg/L, 176 ppm, 240 ppm, and 4.98%, respectively, under 25% load conditions. As the load increases, combustion is perfected, CO and HC emissions gradually decrease, and the percentage of CO_2 emissions gradually increases. The CO concentration was 55 ppm and the HC concentration was 172 ppm in the exhaust gas under 90% load conditions. However, particulate matter emissions did not decrease with the increasing load, with 0.051 mg/L, 0.035 mg/L, and 0.013 mg/L for 50%, 75%, and 90% load conditions, respectively. Relatively high particulate emissions resulted from 75% working conditions and relatively minimal particulate emissions from 90% working conditions. Moreover, the percentage of particulate matter emissions of different diameters from the marine engine varied for each of the working conditions, as shown in Figure 4.

Table 3. Raw emission parameters of the WARTSILA W20DF marine engine.

Load %	**Power kW**	**Exhaust Temperature after Turbine K**	**O_2 %**	**CO_2 %**	**CO ppm**	**HC ppm**	**NOx ppm**	**NO ppm**	**Particulate Matter mg/L**
25	230	650	14.25	4.98	176	240	849	768	0.024
50	450	650	12.3	6.12	92	234	1003	910	0.051
75	680	600	12.6	5.9	61	208	935	856	0.035
90	810	585	12.66	5.86	55	172	880	800	0.013

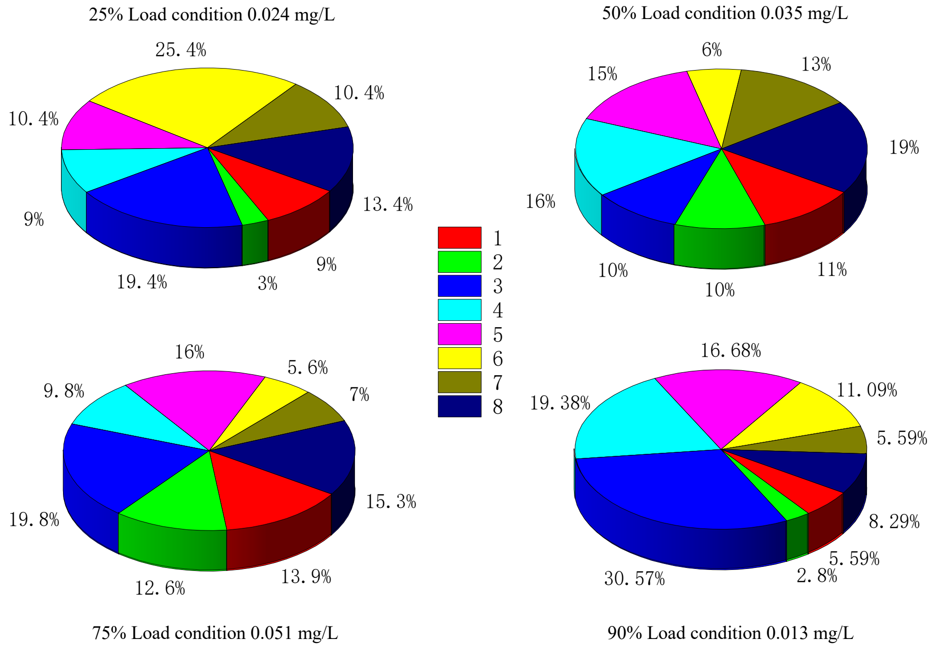

Figure 4. Percentage of particulate matter of different diameters under different working conditions.

The corresponding diameter sizes of particle matter in Classes 1 to 8 in Figure 4 are shown in Table 2. Under 25% load conditions, the 6-micron particle matter comprised about 25.4%, and the 3-micron particle matter comprised about 19.4%. Moreover, the proportions of particles of all diameters were similar under 50% load conditions. Under 75% load conditions, 6–7-micron particles were only about 13%, with similar proportions to other particles. Under 90% load conditions, 3–5-micron particle matter comprised almost 76%. The emission of small-diameter particulate matter was higher under high load conditions.

4.3.2. Carbon Removal Effect of DOC + CDPF

(1) Carbon particle test using Tisch 10-8xx

From the analysis of the test results with Tisch 10-8xx, it can be seen that the carbon particulate removal efficiency of the WARTSILA W20DF marine engine is about 50% under 25%, 50%, 75%, and 90% operating conditions. The detailed data are shown in Figure 5. Under 50% working conditions, the weight of the carbon particles collected behind the DOC + CDPF for 10 min was 6.5 mg, which is 7.76 mg less than the original carbon particle emissions, and the carbon removal efficiency was 54.67%. Its carbon capture under 50% working conditions was greater than that under the other 3 working conditions. The carbon particulate emission was only reduced by 2.1 mg under 90% working conditions with DOC + CDPF, but the removal efficiency was 58.33%, which is slightly higher than that under 50% working conditions. The main reason is that under high load conditions, the combustion efficiency of the WARTSILA W20DF is better and the total amount of carbon particulate emissions is lower. As seen in Figure 6, emissions of particulate matter of different sizes were reduced by different degrees under different working conditions. For example, 5.8–9.0-micron and 3.3–4.7-micron carbon particles at 25%, 1.1–2.1-micron particles at 50% and 75%, and 5.8–9.0-micron and 0.65–1.1-micron particles at 90% were not reduced, but rather the weight of a certain size of carbon particulate matter was increased. This is inextricably linked to the capture of carbon particles and the complex chemical reaction process in the catalytic redox reaction by DOC + CDPF.

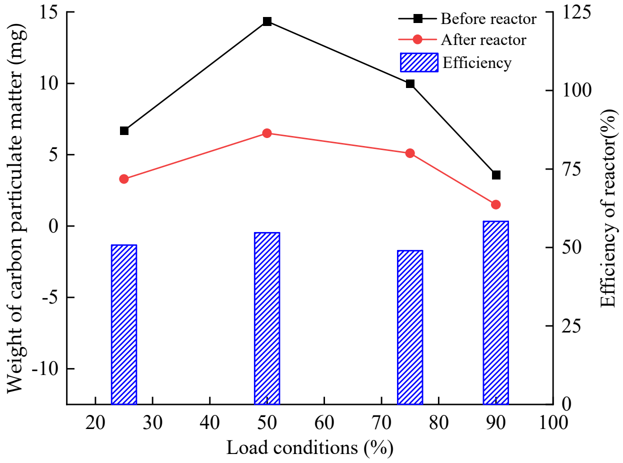

Figure 5. Carbon particle removal effect of DOC + CDPF with Tisch 10-8xx detection.

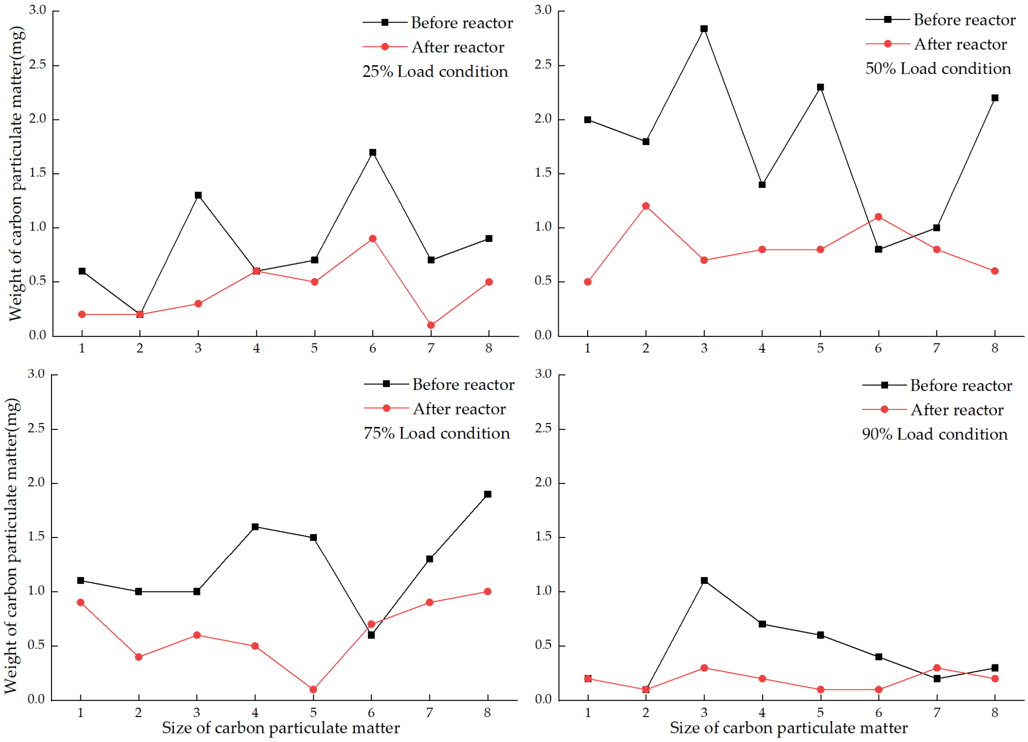

Figure 6. Carbon particle weights of different diameters before and after DOC + CDPF under different working conditions.

(2) Carbon particle test using AVL SPC 478

The AVL SPC 478 is capable of retaining carbon particle matter above 0.3 microns, which is smaller than Tisch's 0.43 microns. The flue gas was sampled for 20 min under each condition, and the color of the carbon particles on the filter paper gradually became lighter as the load increased. It can also be seen in Figure 7 that the color of the carbon particulate matter trapped by the filter paper after the DOC + CDPF reactor was lighter than that before the reactor. The mass of the carbon particulate matter retained for 20 min was calculated by weighing, as shown in Figure 8. The mass of carbon particulate matter retained before the DOC + CDPF reactor was 0.49 mg, 0.67 mg, 0.33 mg, and 0.21 mg under 25%, 50%, 75%, and 90% working conditions, respectively, and that retained after the DOC + CDPF reactor was 0.23 mg, 0.29 mg, 0.15 mg, and 0.1 mg, respectively. The mass change pattern of the carbon particulate matter detected with AVL SPC 478 under the different working conditions of WARTSILA W20DF was consistent with the Tisch 10-8xx's detection values. Moreover, the carbon particulate removal efficiency of DOC + CDPF was also around 50% for all operating conditions. The efficiencies of the 50% and 90% operating conditions were 57.44% and 53.27%, respectively, which are slightly different from the efficiencies obtained from the Tisch detection values.

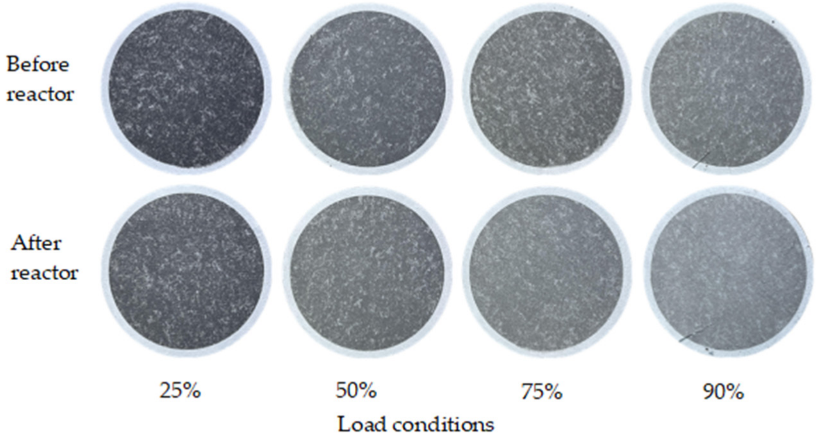

Figure 7. Carbon particles collected before and after DOC + CDPF under different working conditions.

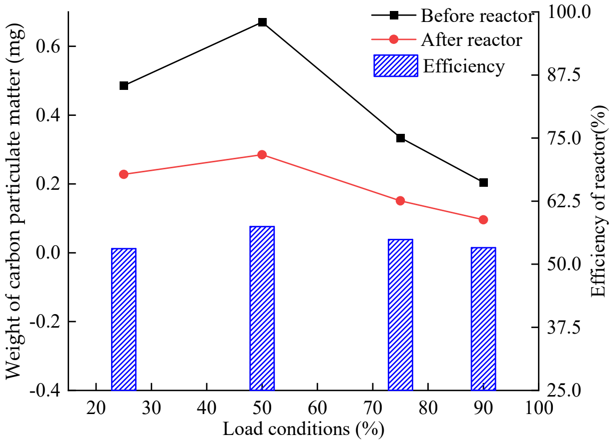

Figure 8. Carbon particle removal effect of DOC + CDPF with AVL SPC 478 detection.

As a result, the efficiency of the DOC + CDPF reactor coated with non-precious metal catalyst regarding carbon particle matter removal from the exhaust gas of the WARTSILA W20DF marine engine was only about 50%. The main reason is that the exhaust temperature of the engine was low, the gas temperature of the DOC + CDPF reactor inlet was not higher than 650 K under all working conditions, and the activity of the non-metallic catalyst coating was relatively low. Therefore, to further improve carbon particulate matter removal efficiency, the reactor needs to be made larger, the reactor inlet flue gas temperature needs to be increased to improve the catalyst activity, or a catalyst with higher activity at a lower temperature needs to be found.

(3) Emissions test using AVL i60

After DOC + CDPF treatment, not only the carbon particulate emissions were reduced but also the HC and CO in the exhaust gas. The emission data based on the AVL i60 analysis of the exhaust gas composition are shown in Figure 9. HC emissions were reduced by about 28%, and CO emissions were reduced by more than 30%. With the catalytic oxidation of the carbon-containing compounds, the oxygen in the exhaust gas was consumed to produce carbon dioxide. NOx concentration was not influenced by DOC + CDPF, but the NO value increased. These research results have an important reference value for the optimization of DOC + CDPF.

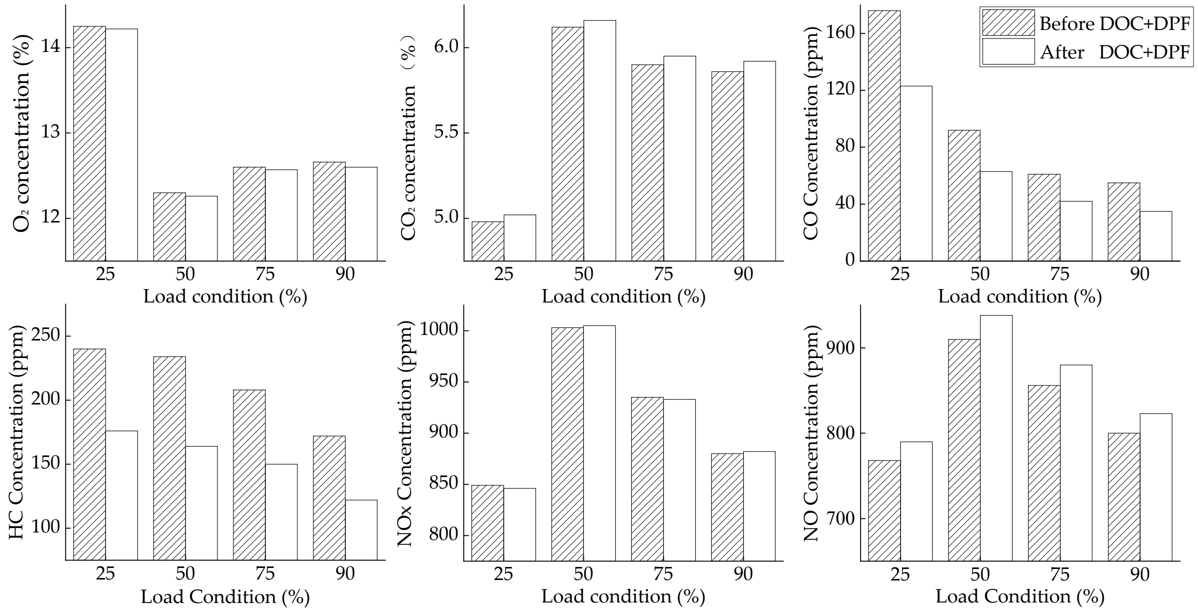

Figure 9. Analysis of the composition of exhaust gas before and after DOC + CDPF with AVL i60.

5. Conclusions

This study analyzed the carbon particulate matter removal efficiency of a type of non-precious metal catalyst coating at different temperatures and verified the efficiency of the DOC + CDPF reactor with this type of catalyst for carbon particulate removal from WARTSILA W20DF exhaust gas, which was operated under four different conditions with a diesel oil combustion model. Based on the analyses elaborated above, the main conclusions of the study are as follows:

(1) With this type of non-precious metal catalyst, the combustion rate of carbon particulate removal increases with temperature. The combustion rate was only 3 mg/s at about 600 K, up to 12.5 mg/s at 800 K, and the combustion efficiency was higher than 20 mg/s at 900 K.

(2) NOx in the gas can improve the combustion rate of carbon particulate matter, and the rate increases significantly after the NOx concentration reaches 1350 ppm.

(3) According to the amount of carbon particulate matter retained by the filter paper at the same time, the highest amount of carbon particulate matter in the exhaust gas of the WARTSILA W20DF marine engine appeared under 50% working conditions and the least amount under 90% working conditions.

(4) The DOC + CDPF reactor in this study achieved 50% efficiency for the removal of carbon particulate matter from WARTSILA W20DF exhaust gas. In the later studies, the reactor size, flue gas temperature, or low-temperature catalyst was optimized to further improve the carbon particulate removal efficiency.

As mentioned above, the carbon particulate matter removal efficiency is not optimal because of the influence of the exhaust gas temperature. How to increase the exhaust gas temperature or find a lower-temperature catalyst is the focus of the next stage of research. In addition, the efficiency of this type of catalyst for the removal of carbon particulate matter emissions from marine diesel engines using heavy oil also needs to be investigated. This will provide a reference for solving the carbon emission problem of ships under carbon emission requirements.

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