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## A Short Review of Treatment Methods of Marine Diesel Engine Exhaust Gases

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### Abstract

Marine diesel engine mainly use heavy fuel oil with high-sulfur as fuel, making its main pollutants become nitrogen oxides( $\text{NO}_x$ ), sulfur oxides( $\text{SO}_x$ ) and particulate matters(PM). It's urgent to reduce the pollutants using advanced technology. Herein, we reviewed the treatment methods of marine diesel engine exhaust gas, especially for  $\text{NO}_x$  and PM treatment.

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### 1. Introduction

With the rapid development of economy and trade, ship emissions are increasing in the meantime. Because of the hazardous gases, regulations and legislations have become much stricter recently. International Maritime Organization (IMO) passed Marine Pollution (MARPOL) Annex VI, Regulations for the prevention of air pollution from ships. And

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it is revised on the 58th meeting of the Marine Environment Protection Committee (MEPC) in 2008. The regulations formulate the most stringent NO<sub>x</sub> legislation, IMO Tier III, and the stringent legislation of fuel sulfur content.

Diesel engine belongs to compression ignition reciprocating internal combustion engine, which decides it can use the less volatile diesel or poor quality fuel oil as propulsion. Marine diesel engine mainly use heavy fuel oil with high-sulfur as fuel, which leads to its main pollutants are nitrogen oxides(NO<sub>x</sub>), sulfur oxides(SO<sub>x</sub>) and particulate matters(PM) [1-3]. Since the generation mechanism of NO<sub>x</sub> and PM showed the opposite effect, namely a reduction in one emission will lead to the other emission increase [4], this creates more difficulty for controlling the emission of marine diesel engine. Thus, it's urgent to develop new technologies to limit the exhaust of hazardous gases from the ships. Herein, we reviewed the development methods of hazardous gas exhausted from marine diesel engines in recent years, especially reducing NO<sub>x</sub> and PM.

## 2. PM treatment

Currently, the technology of reducing particulate matters (PM) from marine diesel engines is not mature enough [5]. Particulate matters treatment can be categorized into Diesel Particulate Filter (DPF), Diesel Oxidation Catalyst (DOC) and Continuous Regeneration Trap (CRT). DPF technology can reduce the exhaust soot particles and it is recognized an effectively reduce diesel particulate emissions. The principles of DPF technology includes inertial impaction, interception, diffusion and sedimentation theory [6]. Because the process is a physical process, with extended filter time, particles can settle on the filter surface, making filtration efficiency reduced to a certain extent, so the key to DPF technology is filter body regeneration. Currently honeycomb ceramic wall-flow particulate trap particulate matter filtration efficiency can be up to 90% [4,6]. Danish Notox company developed a novel SiC honeycomb structure wall-flow filters, the filtration efficiency of which can reach 99.8%; Per-Tec's Power trap particulate particle filter efficiency is 70%, the UK Piccadilly road transport companies have applied this type of filter [7].

The main function of DOC is to oxidize the hazardous pollutants in the exhaust gas. Liang[6]'s report showed that when the exhaust gas pass through the catalyst, hydrocarbons and carbon monoxide can react with O<sub>2</sub> forming H<sub>2</sub>O and CO<sub>2</sub> without pollution. But this technology is only appropriate for the diesel with low sulfur component, because oxidation reaction can make SO<sub>2</sub> turn into SO<sub>3</sub>, then SO<sub>3</sub> will react with water then convert into sulfates. Hou<sup>[8]</sup>indicated that oxidation catalytic technology eliminates PM through oxidizing the soluble substances, meanwhile CO emissions of diesel engines reduce 30%, HC emissions reduced 50%.

Continuous regeneration trap (CRT) is consist of DOC and DPF, as shown in Figure 1. The former is used to purify HCs, CO and oxidize NO<sub>x</sub>, the latter can filter and collect the particulates. The effect of purification of particulates mainly performs on the continuous passive regeneration process, exhaust temperature decides the CRT can regenerate or not, if lacking of the regeneration process, particulates only can be oxidized above 500°C [9]. H.Y. Liu [10]'s experiment research indicated that when the volume ratio of DOC / DPF approaching 1.5, CRT regeneration rate is ideal. CRT system needs to use the diesel without sulfur or low sulfur, so now it is still difficult to use CRT on the ship, but it has been used in diesel vehicles. CRT will have a bright future when the heavy diesel oil standard is more strict.

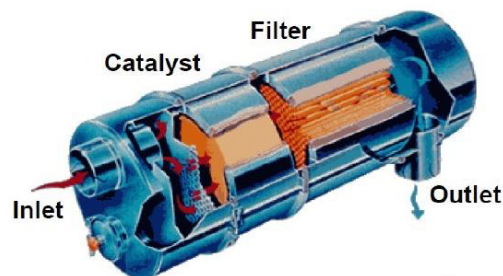


Fig. 1. Continuous Regeneration Trap [10].

### 3. NO<sub>x</sub> treatment

Selective catalytic reduction (SCR) has been widely used in power plants, diesel vehicles and other diesel engines. It is considered the most promising way to meet the most strict Tier III standard. For SCR system process, the most important issue is catalyst. Most of the catalyst of marine SCR in use is V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub>. Figure 2 shows the marine SCR system of Hitachi Zosen Corporation. Other ways such as exhaust gas recirculation (EGR), non-thermal plasma (NTP) and lean NO<sub>x</sub> traps (LNTs) have also investigated by researchers.



Fig. 2. Marine SCR system (Hitachi Zosen Corporation ).

Seo and Choi [11] compared two kinds of Fe-zeolite with V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub> catalyst using hydrocarbons as reducing agent to remove exhaust gas from ship engines. The results show that due to Brønsted acid sites, V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub> suffered the least sulfur poisoning and the NO<sub>x</sub> conversion rate is relatively higher at about 350°C. Japke et al. [12] also test the performance of V<sub>2</sub>O<sub>5</sub> – WO<sub>3</sub> – TiO<sub>2</sub> catalyst prepared by incipient wetness impregnation. The results showed that synthesis method had a strong effect on the SCR of NO<sub>x</sub> and on both the propylene and soot oxidation activity.

Zhou et al. [13] studied an extruded commercial monolithic V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst of marine SCR system at low temperatures. The results showed that SCR reaction is mainly affected by internal chemical reaction kinetics when T<150°C, when T>200°C, reactant diffusion rate will primarily affect SCR reaction. The NO<sub>x</sub> reduction can be improved by controlling space velocity, increasing NH<sub>3</sub> consumption appropriately, excess O<sub>2</sub> and NO<sub>2</sub> concentration in the gas mixtures.

Magnusson et al. [14] researched the influence of sulfur, water and low temperature on commercial SCR V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub> catalyst in marine applications, using urea as reducing agent. It was concluded that high NO<sub>x</sub> reduction could be above 90% at temperatures above 300°C.

EGR of NO<sub>x</sub> purification fundamentals is in the case of a constant heat of fuel combustion, mix the exhaust gas with air and fuel, thereby reducing the maximum combustion temperature. It is belonging to the machine processing technology [15]. Agarwal et al. [16] investigated EGR by returning a proportion (typically 20%) of exhaust gas back to the inlet, which leads to reduction in the peak cylinder temperature, reducing NO<sub>x</sub> production by up to 50%. EGR is related with a rise in PM, CO and HC emissions while exhaust gas temperature is decreased [16]. Figure 3 shows a schematic diagram of engine setup using EGR.

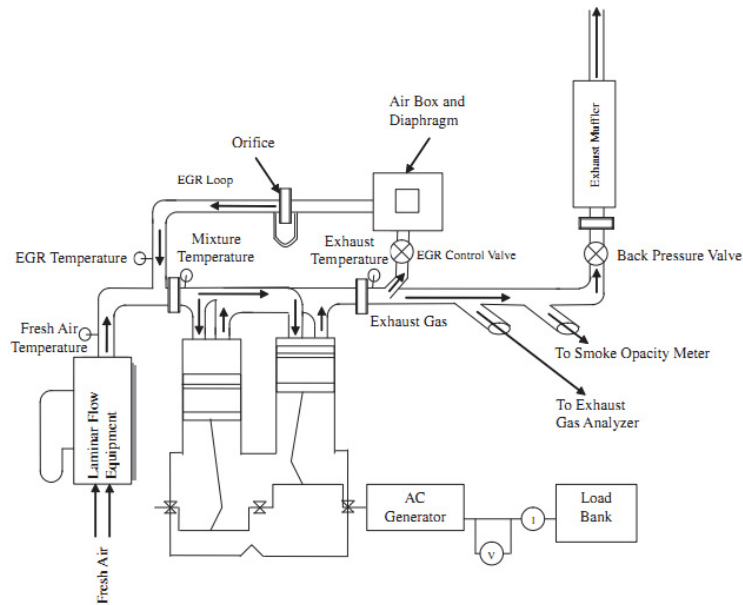


Fig. 3. Schematic diagram of engine setup using EGR [16].

Kuwahara [17] investigated when applying NTP to marine diesel engine pilot-scale experiments, the results showed that the supporting role of  $\text{NO}_x$  adsorption and desorption can make the denitration result meet strict standards of IMO. This system consists of marine diesel engine, DPF, adsorption chamber and NTP reactor, which is shown in Figure 4.

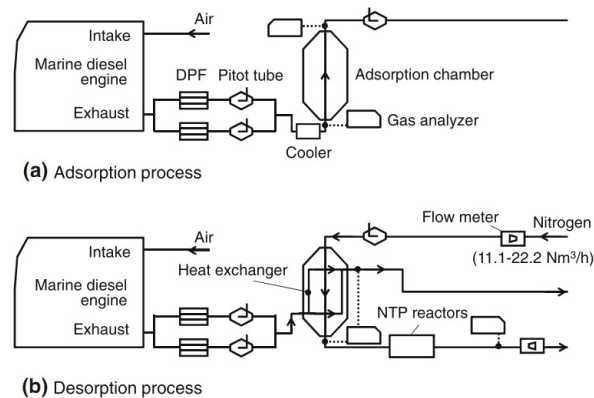


Fig. 4. Marine diesel engine exhaust using NTP treatment process [17].

Zheng [18] used high concentration of oxygen active particle prepared by strong ionic discharge injecting marine diesel engine channels, the results showed  $\text{NO}_x$  removal efficiency greater than 95%. When Yu [19] researched on NTP used into desulfurization and denitrification of marine diesel engines, the experiment result showed that with the plasma power supply fully opening, 17% oxygen content in the air, adding humidifier water, activating wet scrubbing device,  $\text{NO}$  removal rate was over 70% while  $\text{SO}_2$  removal efficiency exceeded 90%.

#### 4. Discussions and Conclusions

- The main challenges for marine SCR applications are sulfur resistance and low temperature activation [14]. Currently, SCR catalyst mainly relies on V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub>, but V<sub>2</sub>O<sub>5</sub> is a kind of highly poisonous material and the active temperature is above 300 °C. We can change this situation by developing novel catalyst with sulfur resistance and low temperature activation, such as other types of rare earth oxides, zeolites and combination of different types.
- The size of NH<sub>3</sub>-SCR system in use is also a problem, urea is usually used to instead of NH<sub>3</sub> because of the difficulty to store. Researchers have indicated that the urea consumption of SCR system is 8.5% of the consumption of diesel oil [20], which will surely add to the size and weight. SCR for marine applications are usually not placed in combination with DPF or DOC, but sometimes an oxidation catalyst can be placed downstream of the SCR in order to reduce the NH<sub>3</sub>-slip and also the CO emissions [14]. NH<sub>3</sub>-slip is also important in SCR use [21]. Tan and Lin [22] indicated the space velocities (SV), exhaust temperature and NH<sub>3</sub>/NO<sub>x</sub> ratio had effects on saturated ammonia storage and time. So changing the reducing agent is also a considering way to treat NO<sub>x</sub>, in this way it may reduce the size and allow the DPF or DOC to treat particulate matters from the exhaust gas. But DOC can't be placed upstream of the SCR avoiding oxidizing SO<sub>2</sub> to SO<sub>3</sub>.
- If the rapid SCR reaction occurs in the system, that is NO/NO<sub>2</sub> is approximately 1, using the oxidation catalyst to oxidize NO to NO<sub>2</sub> [23,24]. That may also reduce the size of SCR system to some degree.
- EGR can't be used to deal with exhaust gas separately, but it can assist other technologies. Only using EGR can't meet the strict standard of IMO. If the rapid SCR reaction occurs in the system, that is NO/NO<sub>2</sub> is approximately 1, using the oxidation catalyst to oxidize NO to NO<sub>2</sub> [23,24]. That may also reduce the size of SCR system to some degree.
- When dealing with NO<sub>x</sub> pollution compared with SCR technology, NTP has the advantage of not using the catalyst, urea or other reducing agent, reaching zero-pollution emissions [18] and the operating temperature can be lower than 150 °C [17]. But main disadvantages of NTP technology is high energy consumption and expensive prices of electronic accelerator [23] and it will have a low treatment efficiency in the condition of excess O<sub>2</sub>.

To conclude, SCR is still the most promising way to reduce NO<sub>x</sub>, we could try to find new economic catalyst with good sulfur resistance and low temperature activity instead of V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>–TiO<sub>2</sub>, try to minimize the volume of SCR to combine with DPF or DOC in the future. As sulfur content of fuel oil is limited by IMO, then low temperature SCR catalyst will have a more easy way to get in use, also, it could effectively reduce the impact of shipping to primary particles [25].

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