Pollution Control of Exhaust Emissions of Marine Diesel Engines

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Abstract. This paper describes the impact of marine diesel engine exhaust gas on the atmospheric environment and the international control requirements for marine diesel engine emissions internationally; introduces the current technical measures to reduce emissions of diesel engine exhaust pollution. On this basis, the advantages and disadvantages of each measure and the application scopes are explored.

Keywords: Marine diesel engine, exhaust emissions, emission control.

1. Introduction
At present, how to improve the reliability and reduce fuel consumption of diesel engines, what's more, it is how to reduce their environmental pollution. The reason why the diesel engine has become the most important power unit for ships in the world today is that the diesel engine operates safely and reliably, its thermal efficiency is more than 50%. In the past ten years, the fuel consumption rate of diesel engines has dropped by 15% -25%, but NOx emissions have increased by 30% -40% due to the combustion of diesel engines at higher pressure and temperature conditions; moreover, SOx has also increase. With the vigorous development of the world's shipping industry, the emissions of marine diesel engines have caused more and more serious pollution to the atmosphere. In developed shipping countries, 40%-50% of total NOx emissions come from ships, these pollutants cause environmental degradation and will definitely endanger the survival of humans and other organisms. Therefore, we must strictly control the exhaust emissions of marine diesel engines.

2. Hazard of Exhaust Emissions of Marine Diesel Engines
In today's world, people are paying more and more attention to the problems of environmental pollution, and the requirements of the ecological environment are becoming stricter, the requirements for controlling harmful gas emissions of engines are becoming stronger and stronger, and each country has formulated regulations to limit emissions of means of transportation, and emissions regulations are becoming increasingly stricter. With the development of the shipping industry, ship power exhaust emissions have become more and more serious to the atmospheric environment. A medium-speed high-power diesel engine runs 4000h per year and produces about 1500t NOx. The atmospheric pollution of marine engine exhaust gas has aroused worldwide attention, and the potential hazards of marine diesel engine exhaust emissions to the atmosphere have been highly valued by government departments in various countries.
Hazardous substances emitted by diesel engines include: NO\textsubscript{x}, SO\textsubscript{x}, CO, CO\textsubscript{2}, PM, etc. SO\textsubscript{x} can cause acid rain, NO\textsubscript{x} is the main factor that forms acid rain and fog, which is not good for human health, and N\textsubscript{2}O has a strong destructive effect on the ozone layer, CH\textsubscript{4}, CO\textsubscript{2}, etc. can cause greenhouse effect, and the toxicity of CO is well known.

The NO\textsubscript{x} in diesel exhaust gas comes from two aspects, one is that the oxygen is oxidized at high temperature in the air, and the other is the nitrogen compounds in the fuel all are oxidized to NO\textsubscript{x}, which accounts for about 20%-30% of NO\textsubscript{x} in the exhaust gas. The chemical reaction process of NO\textsubscript{x} generated by N\textsubscript{2} in the air is complicated, and it has a great relationship with temperature and reaction time. The higher the temperature, the more NO\textsubscript{x} is generated, usually, Normally, every time the temperature rises by\textdegree C, NO\textsubscript{x} emissions will double, the longer the reaction time, the different the content of NO\textsubscript{x}. Tests show that as the cylinder bore increases, NO\textsubscript{x} increases: the lower the speed, the higher the NO\textsubscript{x}. Therefore, when the cylinder bore increases, the more difficult it is to reduce NO\textsubscript{x}, and the reduction of NO\textsubscript{x} tends to increase the fuel consumption of the diesel engine. Therefore, how to reduce the NO\textsubscript{x} emissions of diesel engines without increasing fuel consumption is a future research topic.

The generation of SO\textsubscript{x} in exhaust gas is mainly related to the sulfur content in fuel oil. During the combustion process, all the sulfur in the fuel is oxidized to SO\textsubscript{x}. However, reducing the fuel content of the fuel will increase the price of the fuel. In addition, sulfur helps improve cylinder lubrication. Therefore, the use of low-sulfur fuel may affect the lubrication of the cylinder. Reduction of fuel oil content should be solved by oil refineries. Incomplete combustion of hydrocarbon emissions in diesel engines is usually low, sometimes they are caused by some defects in the design of the fuel injection system, such as nozzle pressure, oil cavity volume, etc., but these defects can be eliminated.

After the fuel is burned, the CO\textsubscript{2} produced is fixed. Therefore, in order to reduce CO\textsubscript{2}, we can only reduce the fuel consumption, or reduce the carbon content of the fuel and increase the hydrogen content. At present, the thermal efficiency of diesel engines is the highest among various types of heat engines, so relatively speaking; diesel engines have the lowest fuel consumption and the lowest CO\textsubscript{2} emissions. The particulate matter in diesel exhaust mainly comes from fuel oil and lubricating oil, if refined light oil is used instead of heavy oil, although the particulates in the exhaust gas can be reduced, it is contrary to the improvement of economic efficiency. Increasing the injection pressure and improving the quality of air and fuel mixture can reduce the generation of particulates, but must ensure the reliability of the system. Moreover, reducing the consumption of lubricating oil can also reduce the amount of particles in the exhaust gas. From the above, the main causes of atmospheric pollution in diesel exhaust gas are SO\textsubscript{x} and NO\textsubscript{x}, and NO\textsubscript{x} is the main control object. Fig.1 shows the emissions of MC-type low-speed diesel engines, emission components are mainly NO\textsubscript{x}, SO\textsubscript{x}, CO, CO\textsubscript{2}, and other gases.
3. NOx Generation Mechanism of Diesel Engine

Nitrogen compounds in diesel exhaust include NO, NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O, N\textsubscript{2}O\textsubscript{5}, etc.). After burning the fuel, about 90%-95% of the nitrogen oxides exhausted from the exhaust pipe are NO; therefore, the nitrogen oxides to be controlled for the internal combustion engine are mainly NO. At present, the NO calculation is widely used with following formulas:

\[
N_2 + O \Leftrightarrow NO + N \tag{1}
\]

\[
N + O \Leftrightarrow NO + N \tag{2}
\]
The forward reaction speed of formula (1) increases rapidly with temperature. The N atom in the formula (2) is supported by the formula (1), and the O atom in the formula (1) is supported by the formula (2). NO concentration in the cylinder is determined by three factors:

Peak combustion temperature, high peak temperature is the first factor under oxygen-rich conditions, otherwise NO generation is suppressed. Is there enough oxygen, there is a high air-fuel ratio but the peak temperature of combustion is not high, and the amount of NO is not much. Whether high combustion peak temperature is maintained for a long time, if long the NO concentration is large. Therefore, if the peak combustion temperature is higher, the air-fuel equivalent ratio is greater than 1, and the exothermic period near the maximum temperature is longer, the NO emission concentration is higher. Fig.1 shows the influence of pressure and temperature on the generation of NO during combustion, namely the higher the pressure and temperature, the more NO emissions. Therefore, we can realize that the generation of carbon monoxide is related to many factors; it is not only related to the structural parameters of the engine, but also related to the operating parameters. In order to reduce the emissions of diesel engines, it is necessary to comprehensively consider the effects of various factors.

4. Method for Reducing NOx of Marine Diesel Engine

At present, there are mainly two methods to reduce the NO\textsubscript{x} content of marine diesel engine exhaust, the combustion control method and the exhaust post-treatment method. The combustion control method is also called as the primary treatment method, it is to reduce the generation of NO\textsubscript{x} during the combustion process, which can reduce by 20%-50% NO\textsubscript{x}, the post-treatment method is to post-process the diesel exhaust gas in a specially set device, which can reduce 70% -90% NO\textsubscript{x}.

4.1. Combustion control method

In order to reduce NO\textsubscript{x} during the combustion process, specifically, the following measures can be taken:

1. Perfect the combustion process, in recent years, marine low-speed diesel engines have conducted a lot of development and research to meet the NO\textsubscript{x} emission standards proposed by IMO, For example, the MAN-B\&W low-speed engine has been continuously improved, and the combustion process of fuel in the engine cylinder has become perfect, compared with the GFC model, the NO\textsubscript{x} in the MC machine is reduced by 22.62% -37.50%.

2. Water-emulsified oil, by mixing fuel with water and emulsifying the oil-water mixture before it flows into the engine, this can reduce by 20% NO\textsubscript{x} emissions without affecting fuel consumption.

3. Spray water into the combustion chamber, which can reduce the maximum combustion temperature and reduce by 10% NO\textsubscript{x} emissions, but may cause corrosion.

4. Higher compression ratio can improves thermal efficiency and reduce fuel efficiency. Although the high combustion temperature increases NO\textsubscript{x}, the actual emissions are reduced due to the improved thermal efficiency.

5. Increase the boost pressure, which reduces the fuel consumption and exhaust temperature, improves engine performance, and reduces NO\textsubscript{x}.

4.2. Post-treatment method:

At present, generally, it is required that NO\textsubscript{x} emissions should be reduced to 10pm under the condition of 15% oxygen, this has been implemented in some coastal waters, and it is believed that such NO\textsubscript{x} emission levels will be generally implemented in recent years. In the currently mature technology, high-efficiency diesel engines can reach such NO\textsubscript{x} emission levels only through catalytic converters.

Due to the large air ratio used in diesel engines, automobile-type catalysts cannot be used. After short-term operation, heavy metals and sulfur elements in heavy oil will deteriorate the deterioration of automobile catalysts. However, by using selective catalytic reduction (SCR) to Reduction of NO in exhaust gas is still feasible. A schematic diagram of the SCR process using selective catalytic reduction to reduce NO\textsubscript{x} is shown in Fig.3.
The main components of catalytic reduction process are reactor equipped with catalyst and an ammonia addition system. The ammonia source can be anhydrous liquid ammonia under pressure, or aqueous ammonia solution under atmospheric pressure. Ammonia water is evaporated in an evaporator and then diluted with air; these processes are done before the mixed gas is injected into the exhaust pipe. The exhaust gas passes through the catalyst at 300-400°C temperature, NO\(_x\) is restored to N\(_2\) and H\(_2\)O, its specific reaction process is as follows:

\[
4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} + 1809.7\text{kJ}
\]

\[
8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} + 2735.3\text{kJ}
\]

Although it is selective catalytic reduction, side reactions also occur under certain conditions, for example:

\[
4\text{NH}_3 + 3\text{NO}_2 \rightarrow 7\text{N}_2 + 6\text{H}_2\text{O} + 1267.1\text{kJ}
\]

\[
2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 + 91.94\text{kJ}
\]

\[
4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} + 907.3\text{kJ}
\]

The first side reaction occurs at 623K temperature, and the latter two side reactions increase significantly when they are above 723K. Therefore, it is important to control the reaction temperature, and it is advisable to control the reaction temperature below 573K. However, it should not be too low, so as not to cause the reaction rate to be too low; and catalysis may be damaged due to condensation. The catalyst must be properly selected, so that the main reaction has an absolute advantage to facilitate the removal of NO\(_x\). The catalyst of selective catalytic reduction method mainly uses titanium oxide as carrier, and some use zeolite catalyst. By using the SCR method, more than 95% NO\(_x\) can be reduced. In addition, some soot and hydrocarbons in the exhaust can be removed by oxidation in the SCR reactor.

5. Conclusion

Exhaust emissions of marine diesel engines, especially NO\(_x\) emissions, are important indicators affecting living environment. In order to protect the environment, controlling the emission levels of marine diesel engines has become an urgent problem that needs to be solved. For this purpose, ship management recognizes the importance of controlling exhaust pollution; strengthens the management of marine diesel engine operation, through various technical means, so as to reduce exhaust pollution of marine diesel engine.
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