


Review

Application and Development of Selective Catalytic Reduction Technology for Marine Low-Speed Diesel Engine: Trade-Off among High Sulfur Fuel, High Thermal Efficiency, and Low Pollution Emission

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Abstract: In recent years, the International Maritime Organization (IMO), Europe, and the United States and other countries have set up different emission control areas (ECA) for ship exhaust pollutants to enforce more stringent pollutant emission regulations. In order to meet the current IMO Tier III emission regulations, an after-treatment device must be installed in the exhaust system of the ship power plant to reduce the ship NO_x emissions. At present, selective catalytic reduction technology (SCR) is one of the main technical routes to resolve excess NO_x emissions of marine diesel engines, and is the only NO_x emission reduction technology recognized by the IMO that can be used for various ship engines. Compared with the conventional low-pressure SCR system, the high-pressure SCR system can be applied to low-speed marine diesel engines that burn inferior fuels, but its working conditions are relatively harsh, and it can be susceptible to operational problems such as sulfuric acid corrosion, salt blockage, and switching delay during the actual ship tests and ship applications. Therefore, it is necessary to improve the design method and matching strategy of the high-pressure SCR system to achieve a more efficient and reliable operation. This article summarizes the technical characteristics and application problems of marine diesel engine SCR systems in detail, tracks the development trend of the catalytic reaction mechanism, engine tuning, and control strategy under high sulfur exhaust gas conditions. Results showed that low temperature is an important reason for the formation of ammonium nitrate, ammonium sulfate, and other deposits. Additionally, the formed deposits will directly affect the working performance of the SCR systems. The development of SCR technology for marine low-speed engines should be the compromise solution under the requirements of high sulfur fuel, high thermal efficiency, and low pollution emissions. Under the dual restrictions of high sulfur fuel and low exhaust temperature, the low-speed diesel engine SCR systems will inevitably sacrifice part of the engine economy to obtain higher denitrification efficiency and operational reliability.

Keywords: SCR system; marine low-speed diesel engine; high sulfur fuel; engine tuning; development trends



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1. Introduction

Based on the consideration of ship operating costs, the ship engines generally burn low-quality fuel. Low-quality fuel oil includes Intermediate Fuel Oil (IFO) and Heavy Fuel Oil (HFO). Low-quality fuel oil is a mixture of Residual Oil (RO) after distillation by petroleum and Marine Diesel Oil (MDO). In a certain proportion, it has high viscosity, high sulfur content, high residual carbon, and heavy metals (cadmium, vanadium, and lead, etc.).

Due to the use of low-quality fuel in ship engines, the exhaust gas emitted by its combustion must contain a large amount of nitrogen oxides (NO_x), sulfur oxides (SO_x),

carbon dioxide (CO₂), particulate matter (PM), volatile organic compounds (VOC), and many other pollutants, causing serious pollution to the marine environment and the port atmosphere. Its emissions are shown in Table 1 [1]. Among them, nitrogen oxides, sulfur oxides, and carbon dioxide are corrosive gases, which can easily cause pollution problems such as acid rain and photochemical smog and exacerbates the greenhouse effect. Additionally, these five pollutants will stimulate the central nervous system and respiratory system of the human body, causing adverse effects on human health. Furthermore, the main emissions from diesel engines are smoke emissions and nitrogen oxides. The reaction between atmospheric nitrogen and smoke emissions occurs at high temperatures, and smoke emissions are high in the oil-rich areas within the engine cylinders. The main challenge for compression ignition engines is to simultaneously reduce smoke and NO_x emissions [2].

Table 1. Pollutant emissions from a typical low-speed diesel engine burning low-quality fuel [1] (unit: g/(kW·h)).

Operating Mode	NO _x	SO _x	CO ₂	PM	VOC
Normal sailing	17	10.5	620	1.7	0.6
Idle or berthing state	13.6	10.6	682	2.4	1.8

According to statistics, marine diesel engines emit about 20 million tons of NO_x, 10 million tons of SO_x, and 1 million tons of PM every year [3]. In addition, NO_x, SO₂, and CO₂ emissions from ships account for 15%, 4–9%, and 2.7% of global anthropogenic pollution, respectively [4]. With the development of shipping industry and trade, ship power plants have become one of the main air pollution sources, and the removal of nitrogen oxides is still the core of ship exhaust pollution control.

However, recent surveys have shown that ships take longer in transit because they do not route close to the coast and emit a wider range of pollutants. As a result, global and regional gaseous pollutants including carbonaceous species, PM, carbon monoxide (CO), NO_x, PAHs, hydrocarbons (HCs), SO₂, and VOCs greatly affect the local air quality [5]. Therefore, in order to improve the emission of marine diesel engines, it is an effective measure to use environmentally friendly alternative new fuels and implement efficient after-treatment system technology under different working conditions. Among the after-treatment systems, Abdulfatah Abdu Yusuf et al. [6] studied the use of diesel particulate filters (DPF), diesel exhaust fluid (DEF), and selective catalytic regulation (SCR) to effectively regulate ultrafine particles (UFP), PM, HC, and NO_x emissions so as to achieve MARPOL Annex VI and US EPA Tier III-IV emission standards for marine diesel engines Category 1–2.

In order to reduce the pollution of the ship exhaust to the environment and the atmosphere, the IMO, Europe, and the United States and other countries have formulated strict regulations on ship exhaust pollutants. They also enforce stricter NO_x and SO_x emission standards in designated emission control areas, which directly affects relevant ports and routes in Europe and North America. At the same time, the Ministry of Transport of China established the Pearl River Delta, Yangtze River Delta, and Bohai Rim (Beijing–Tianjin–Hebei) waters as the ship air pollutant emission control areas in 2016 [7].

In order to meet the current IMO Tier III emission regulations, an after-treatment device must be installed in the exhaust system of the ship power plant to reduce the ship NO_x emissions. Currently, SCR technology and exhaust gas recirculation (EGR) technology are the most practical technologies to solve NO_x emissions of marine diesel engines and make them meet the IMO Tier III standard [8]. However, in terms of technology maturity and scope of application, SCR technology is the only NO_x reduction technology recognized by the International Maritime Organization that can be used for various ship engines and ship types.

As western countries began to study SCR technology very early, they have mastered the more advanced marine diesel engine SCR technology, and many products have already been installed on ships and started to operate. At present, MAN is the only manufacturer that can simultaneously provide high-pressure SCR (HP-SCR) and EGR treatment solutions. In 2011, the MAN company cooperated with Hitachi Zosen Corporation to develop a marine high-pressure SCR system, which was verified on the 6S46MC-C8 diesel engine. On 25 February 2019, MAN announced its first order for HP-SCR products: MES m ordered three HP-SCR units for the construction of three 87k DWT bulk carriers to meet IMO Tier III emission standards for their engines [9]. WinGD is developing a more compact and integrated HP-SCR scheme, where the SCR reactor is located on the engine. Therefore, compared with the standard Tier II engine, this scheme only slightly increases the space requirements in the cabin [10].

Furthermore, the research direction of marine diesel engine SCR technology mainly includes the design of the flow field structure of the SCR system, the optimization and the control strategy of the urea spray model, the structural performance of the reaction catalysts, and the structure optimization of the SCR mixer and the SCR reactor. Bartosz Kaźmierski et al. [11] have developed a urea SCR system without a conventional mixer. The system can fully decompose urea and obtain uniform ammonia distribution at the catalyst inlet, while minimizing liquid film deposition and maintaining a compact design. Sadashiva Prabhu et al. [12] pointed out the importance of the mixing zone length and the urea injection point position. If the above parameters are properly defined, more NH_3 may be obtained at the catalyst inlet. Through numerical analysis, it was found that the advantages of increasing the spray angle are enhanced evaporation rate of aqueous solution and increased ammonia concentration. The numerical and experimental analysis carried out by Cho et al. [13] included the arrangement of multiple mixers and decomposition sections to explore the uniformity of ammonia distribution and NO_x conversion efficiency in the Urea-SCR system. The results showed that the application of a static mixer composed of blades significantly improved the ammonia distribution, and the generated turbulent vortex promoted the decomposition of urea aqueous solution (UWS). Steffen Tischer et al. [14] studied the formation and decomposition of liquid and solid by-products that were detrimental to the catalyst in the automotive exhaust pipe using SCR technology through thermogravimetric analysis and differential scanning calorimetry. A new reaction scheme is proposed, which emphasizes the thermodynamic equilibrium of liquid and solid phase reactants. Huang et al. [15] analyzed the formation of liquid film and solid deposit in urea SCR system through numerical simulation. The mixing device was optimized to improve the ammonia uniformity and velocity uniformity at the SCR inlet, and reduce the pressure drop of the system. Some improvements were made in the evaluation indexes considered. In addition, the design reduces liquid film deposition. By analyzing the detailed reaction network framework for the formation of urea deposits, Mo et al. [16] constructed a sub-model of urea decomposition and sediment formation, and calculated the urea decomposition section of the exhaust pipe of the urea-selective catalytic reduction system. The detailed mechanism preliminarily explored can basically reflect the change law of urea conversion to ammonia and some main intermediate products. In view of the fact that the exhaust pipe walls of diesel engine equipped with SCR system easily produces sediment, resulting in the decrease in urea economy and NO_x conversion efficiency, Lv et al. [17] established a simulation model for quantitatively calculating the sediment generation rate of exhaust pipe wall, and revealed the influence of various factors on sediment productivity through single factor simulation.

In conclusion, the published studies on the SCR reaction mechanism mainly focused on low sulfur and low-pressure exhaust gas conditions of diesel engines. However, low-speed diesel engines burn high sulfur inferior residual oil, and the SCR system located in front of the turbine is often in harsh working conditions such as low temperature, high sulfur, and high pressure, which makes the actual operating efficiency much lower than the design efficiency and causes practical problems such as crystallization of ammonium

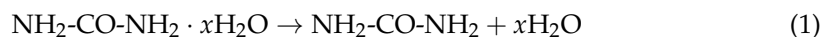
salt. Therefore, the study of SCR reaction mechanism under the limiting conditions of high pressure and high sulfur is an important theoretical basis for solving the practical application problems of low-speed diesel engines. This article discusses the technical characteristics and application problems of the marine SCR systems in detail, tracks the development trend of the catalytic reaction mechanism and engine tuning strategy under high sulfur conditions, and predicts that the development of SCR technology for marine low-speed engines should be the compromise solution under the requirements of high sulfur fuel, high thermal efficiency, and low pollution emissions. Under the dual restrictions of high sulfur fuel and low exhaust temperature, the low-speed diesel engine SCR systems will inevitably sacrifice part of the engine economy to obtain higher denitrification efficiency and operational reliability.

2. Classification of the Marine Selective Catalytic Reduction (SCR) Systems

The marine SCR system is mainly composed of a urea solution injection system, mixer, SCR reactor, measurement system, and soot blowing system [18]. The urea solution injection system is composed of a urea storage tank, urea injection pump, nozzle, valve, and pipeline. Additionally, a static mixer is arranged in the exhaust pipe of the marine SCR system to improve the mixing uniformity of exhaust gas and ammonia gas. It is mainly composed of some baffles with different directions. By changing the airflow direction of the exhaust gas, it causes turbulent flow in different directions. This method can make the urea move and mix rapidly in the radial direction and increase the uniformity of the concentration distribution of the cross-section. Although the mixer can fully mix the exhaust gas and ammonia gas, it will also cause a certain pressure loss. The reactor is the core site for the selective catalytic reduction reaction, which is mainly composed of the reactor shell, catalyst, soot blowing unit, and various sensors. The catalyst in the reactor is generally a modular packaged catalyst, which can be easily replaced. At the same time, the catalyst is installed inside the reactor. The installation position and structure of the catalyst in the reactor can be designed according to the different application sites and space size of the SCR system. By optimizing the design, the mixing uniformity of ammonia gas and exhaust gas can be improved as much as possible.

The selective catalytic reduction technology uses ammonia (NH₃) to reduce NO_x. It selectively reacts with the NO_x in diesel exhaust gas to produce harmless substances N₂ and H₂O within the temperature range of 280–420 °C and under the action of a catalyst, so as to achieve the purpose of removing NO_x [19]. As the urea-water solution (UWS) has no significant harm and the supply system is easy to install, it is widely used as the reducing agent for selective catalytic reduction reactions [20]. At present, the decomposition reaction process of urea is generally simplified to the following reactions:

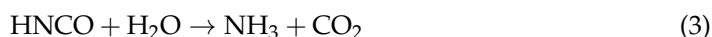
Water evaporation of urea solution:



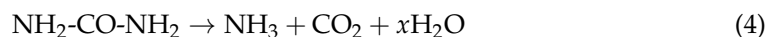
Urea pyrolysis reaction:



Hydrolytic reaction of isocyanic acid:



Therefore, the total reaction of urea decomposition is:



The urea solution is finally decomposed to produce reaction gas NH₃, which is mixed evenly with the tail gas, and enters the SCR reactor for a denitration reaction.

Due to the low exhaust temperature and high sulfur amount of the exhaust gas from the marine diesel engine, the denitration efficiency of the marine SCR system is strongly limited. At present, marine diesel SCR systems, especially two-stroke low-speed diesel SCR systems, mainly achieve higher denitration efficiency by increasing the temperature of the reaction gas to meet the requirements for marine diesel engine emission control [21].

According to the arrangement of the SCR system, the marine SCR system can be divided into the high-pressure SCR (HP-SCR) system arranged in front of the turbocharger and the low-pressure SCR (LP-SCR) system arranged after the turbocharge [22,23]. Figure 1 shows a flowchart of a HP-SCR system and a LP-SCR system on a marine diesel engine.

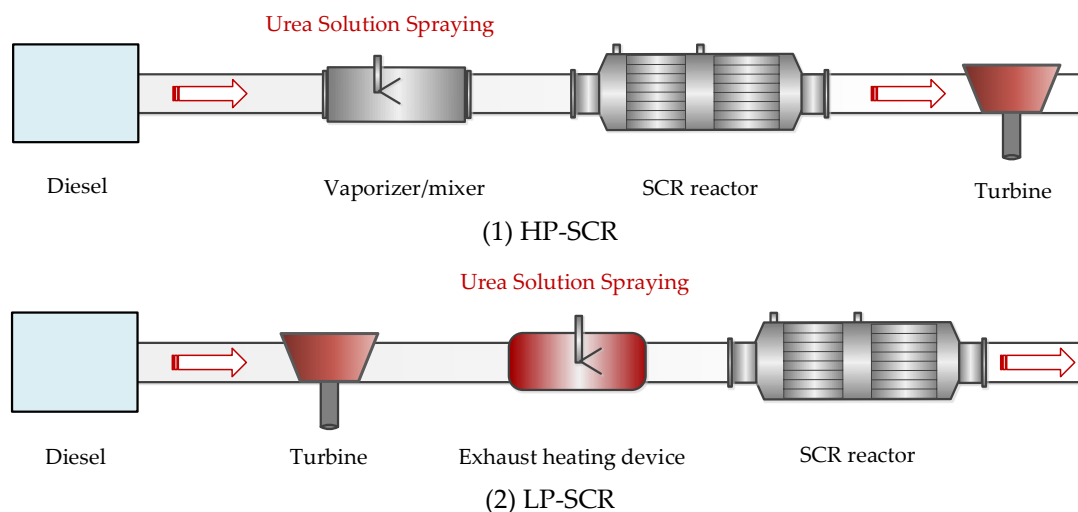


Figure 1. Flowchart of the marine diesel engine high-pressure SCR system and low-pressure SCR system [9].

2.1. High-Pressure SCR System

The HP-SCR system is mainly installed before the diesel turbocharger to fully increase the SCR reaction temperature [24]. This SCR system has a compact layout and high exhaust gas energy utilization rate, but it has a large impact on the working performance of diesel engines and turbochargers [25]. It is mainly used in two-stroke low-speed diesel engines burning high sulfur heavy oil.

Figure 2 shows the HP-SCR system developed by MAN, which mainly includes four parts: vaporizer/mixer, SCR reactor, auxiliary fan, and bypass valve group. The vaporizer/mixer mainly guarantees the complete evaporation and decomposition of the injected urea solution, and ensures the uniform mixing of the reducing agent NH_3 and the exhaust gas. Exhaust gas in the exhaust pipe drives the turbocharger to work, and the exhaust gas temperature before and after the turbocharger differs by 50–175 °C [26]. Therefore, the SCR system in front of the turbocharger can make full use of the higher exhaust gas temperature (low pressure 500 °C) to increase the SCR system denitration efficiency [27].

Figure 3 shows the relationship between the exhaust gas temperature before the turbine and the minimum operating temperature required by the SCR system. It can be seen that when the main engine is running at low load, the temperature of the exhaust gas before the turbine is low and cannot reach the normal working temperature required by the SCR system.

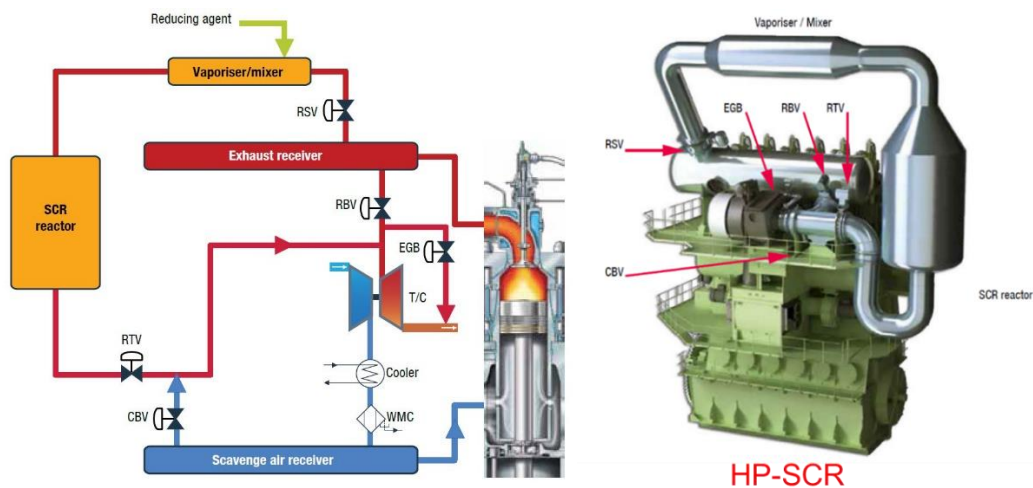


Figure 2. HP-SCR system developed by MAN [18].

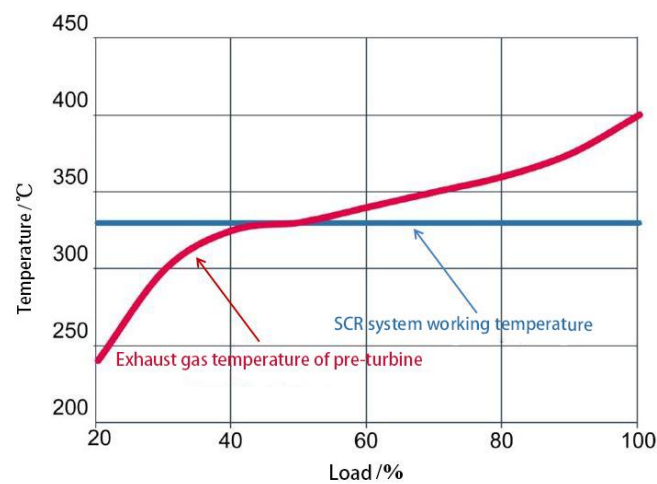


Figure 3. The relationship between the exhaust gas temperature before the turbine and the minimum operating temperature required by the SCR system [18].

In the HP-SCR system, the bypass valve group mainly includes a reactor sealing valve (RSV), a reactor throttle valve (RTV), a reactor bypass valve (RBV), an exhaust gas bypass valve (EGB), and a cylinder bypass valve (CBV). The combination of five groups of pneumatic valves controls whether the exhaust gas flows through the SCR reactor, that is, whether the exhaust gas is treated. For diesel engines that meet the IMO Tier II standard, the switch of the bypass valve group determines the working mode of the diesel engine—Tier II mode or Tier III mode [28]. Additionally, the two working modes of the diesel engine also meet the different emission standards.

In diesel Tier II mode, the RBV is opened, the RSV and the RTV are closed, the exhaust gas directly enters the turbocharger, and the SCR system is inoperative [29–31]. At this time, whether the EGB is opened depends on whether the NO_x emissions of the diesel engine meet the IMO Tier II standard. Generally, the diesel engine produces heavy pollutants at low load, and the EGB ensures that the NO_x emissions of the diesel engine meet the IMO Tier II standard [32]. In contrast, in diesel Tier III mode, the RSV and RTV are opened, the RBV is closed, and the exhaust gas flows through the vaporizer/mixer and SCR reactor and then enters turbocharger, so the SCR system is working.

The exhaust gas temperature often cannot meet the working requirements of the SCR system under low load of diesel engine, even if the SCR system is arranged in front of the turbocharger [33]. To solve such problems, a CBV is arranged between the scavenging collector and the turbocharger inlet to control the amount of fresh air entering the cylinder.

When the CBV is opened, part of the fresh air will flow into the exhaust pipe, and the amount of fresh air entering the cylinder will be reduced, but the scavenging pressure will remain unchanged [34–36]. When the fuel consumption increases, the exhaust temperature of the diesel engine will inevitably increase, and the degree of its increase depends on the increase in fuel consumption [37]. Figure 4 shows the control chart of the bypass valve group.

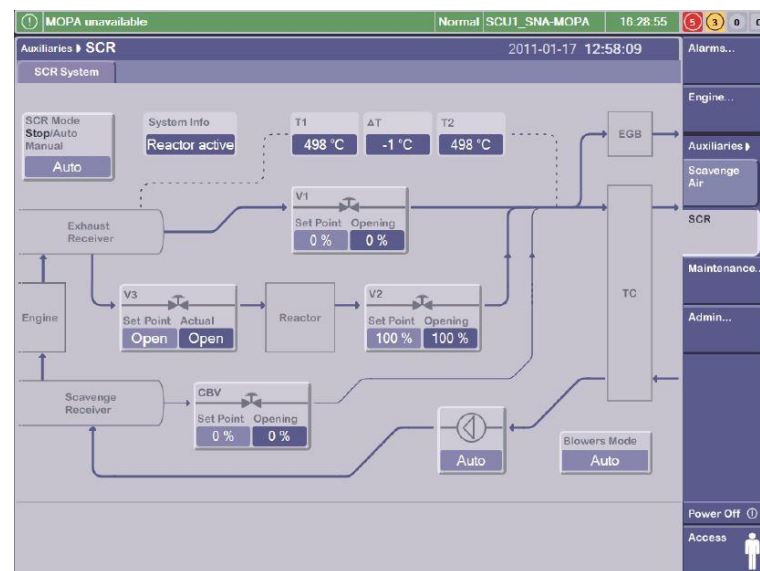


Figure 4. Control chart of the bypass valve group [23].

In diesel Tier III mode, the existence of the vaporizer/mixer and SCR reactor causes a thermal delay between the exhaust gas manifold and the turbocharger [38]. Additionally, the degree of thermal delay mainly depends on the size of the SCR reactor and the heat capacity of the catalyst. This thermal delay will inevitably affect the working performance of diesel engines and turbochargers [39]. The auxiliary fans need to be introduced to ensure the stability of the exhaust pipe [40].

2.2. Low-Pressure SCR System

Compared with the HP-SCR system, the LP-SCR system arranged behind the turbocharger has high adaptability and has less impact on diesel engines and turbochargers [41]. It has been widely used in medium and high speed diesel engines [42,43]. For low-speed two-stroke diesel engines, the denitration efficiency of the LP-SCR system is limited due to its low exhaust temperature [44]. Generally, in the exhaust system of low-speed diesel engines, that is, after the turbocharger and before the SCR reactor, an exhaust gas heating device is installed to increase the exhaust temperature of the diesel engine [45]. At present, there are two commonly used heating methods: electric heating and fuel injection in the exhaust pipe for re-ignition [46,47]. Both heating methods have their advantages, but their equivalent increase in fuel consumption should be controlled within 2.0 g/(kW·h).

Figure 5 shows the LP-SCR system developed by Doosan Corporation, which mainly includes four parts: static mixer (ammonia spray grid), SCR reactor, decomposition unit and bypass valve group. The decomposition unit is connected to the outlet of the SCR reactor and the inlet of the static mixer, and it includes auxiliary fan, exhaust gas heating device (burner) and evaporator [48]. Liquid ammonia or ammonia water is sprayed into the evaporator and mixed with the exhaust gas from blower into the SCR reactor [49].

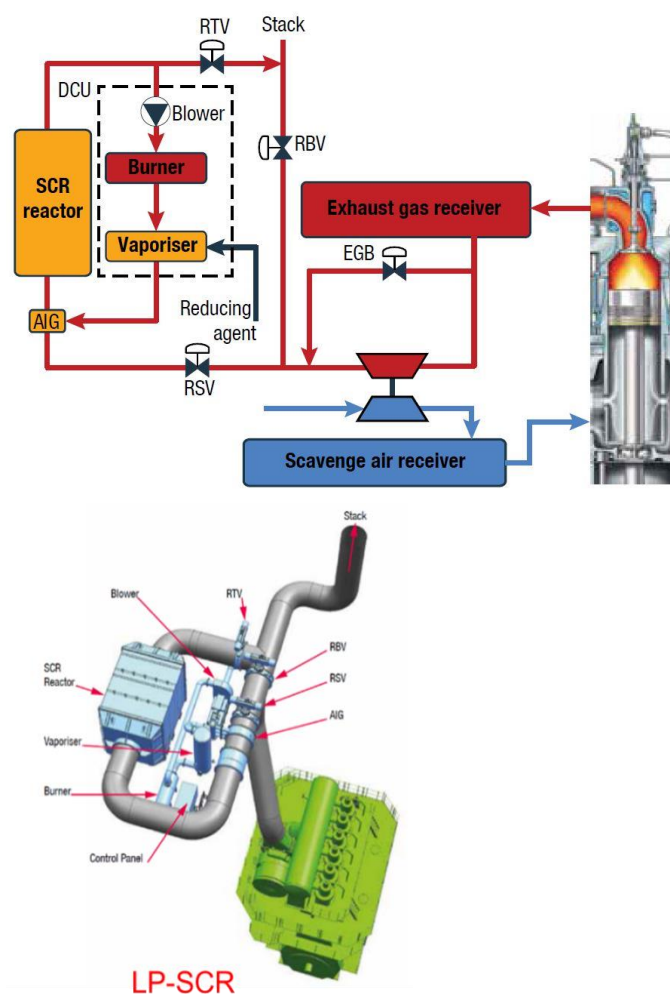


Figure 5. LP-SCR system developed by Doosan Corporation [18].

In the LP-SCR system, the bypass valve group mainly includes a reactor sealing valve (RSV), a reactor throttle valve (RTV), and an exhaust gas bypass valve (EGB). The combination of three pneumatic valves controls whether the exhaust gas flows through the SCR reactor, or whether the exhaust gas is treated. Similar to the HP-SCR system, the diesel engine matching the LP-SCR system also has two working modes—Tier II mode and Tier III mode [50,51].

The exhaust gas temperature after the turbine cannot meet the working requirements of the SCR system under the low load of the diesel engine, even if using the low sulfur fuel. To solve such problems, the CBV is placed between the exhaust manifold outlet and the turbocharger outlet to control the amount of fresh air entering the cylinder. When the CBV is opened, part of the exhaust gas on the high pressure side of the turbine will directly flow into the low pressure side of the turbine, the scavenging pressure will be reduced, and the amount of fresh air entering the cylinder will be reduced. With the increase in fuel consumption, the temperature of diesel exhaust gas will inevitably increase, and the degree of its increase depends on the increase in the fuel consumption. Even if the diesel engine uses low sulfur fuel, the formation of ammonium bisulfate or ammonium bisulfite cannot be completely avoided, but the arrangement of the decomposition unit can alleviate such problems [52].

3. Application Problems of Marine Low-Speed Diesel Engines

Based on the ship operating cost, low-speed marine diesel engines generally burn the inferior residual oil [53]. However, the inferior residual oil often has the characteristics of high viscosity, high sulfur content, high residual carbon, and heavy metals (cadmium,

vanadium, lead, etc.), and its exhaust gas must contain a lot of pollutants such as SO_x (SO_2 and SO_3) and particulate matter (including oil stain). Due to the SO_3 and H_2O in the exhaust gas, the sulfuric acid vapor (H_2SO_4) is easily generated at lower temperatures [54]. When the fuel contains more sulfur, the following three reactions will occur under appropriate conditions:

(1) Fuel burning:



(2) Exhaust gas cooling temperature range of 200–560 °C:



(3) Reaction with water:

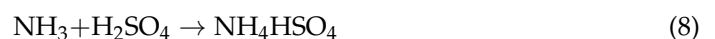


At the same time, as the vanadium-based catalyst (active ingredient: V_2O_5) promotes the oxidation of SO_2 to SO_3 , the concentration of sulfuric acid vapor at the outlet of the SCR reactor is further increased. When the SCR system stops working, or its operating temperature drops below the acid dew point temperature, the sulfuric acid vapor will cool and condense on the exhaust pipe or the reactor wall [55,56]. If it is not discharged in time, long-term accumulation will cause corrosion of the pipeline as shown in Figure 6.



Figure 6. Sulfuric acid corrosion inside the pipeline [28].

During the normal operation of the SCR system, due to the introduction of urea solution, the generated ammonia gas and sulfuric acid vapor will condense into ammonium bisulfate and other substances as shown in Equation (8), causing the amount of sulfuric acid vapor before and after the reactor to be lower [57].



However, the sulfate produced will block the surface structure or pores of the catalyst, resulting in a decrease in catalyst activity. This process is reversible; when the temperature of the exhaust gas rises above the acid dew point, the ammonium bisulfate will decompose and the catalyst activity will be restored [58]. However, if the operating temperature is lower than its acid dew point for a long time, the catalyst activity will permanently change, which will deactivate the catalyst, as shown in Figure 7 [28,59].



Figure 7. Catalyst blocks clogged by scales of rust [28].

The acid dew point temperature of the ammonium bisulfate is usually 280–320 °C, but the low-speed diesel engine has higher thermal efficiency (up to 50%), which results in the lower temperature of its exhaust gas, and the exhaust gas temperature will be lower than the acid dew point temperature of ammonia bisulfate under some operating loads [60]. Therefore, on one hand, it will aggravate the formation of ammonium bisulfate [61]. On the other hand, it will cause the incomplete decomposition of urea at low temperatures and precipitate crystals on the inner wall surface of the pipeline as shown in Figure 8 [62,63].



Figure 8. Precipitation and crystallization caused by urea injection in marine SCR system.

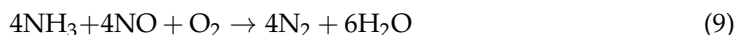
From the perspective of diesel engine operation, using the engine tuning method to increase the diesel exhaust temperature [64], this method will increase the minimum operating temperature of the SCR system or catalyst, which can avoid the formation of sulfate and other deposits. At present, the engine tuning methods mainly include CBV and the turbine EGB [65,66]. By reducing the amount of fresh air entering the combustion chamber and increasing the amount of fuel injected, the exhaust gas temperature is increased at the expense of some fuel economy [67]. Although both methods or means can increase the exhaust gas temperature, it will decrease the power output and fuel economy of the engine, as well as bring about the problem of the turbine matching with the engine [68].

In particular, when the operating loads of the diesel engine change (such as rapid loading or unloading), there may be short-term differences or delays in the exhaust gas temperature before and after the reactor (between the exhaust gas header outlet and the turbine inlet) due to the large thermal inertia of the SCR system catalyst [69]. It will cause energy imbalance before and after the turbine and affect the normal operation of the turbine. Of course, the degree of this thermal delay mainly depends on the size of the SCR reactor and the heat capacity of the catalyst [70,71].

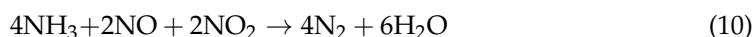
4. Research on Catalytic Reaction Mechanism under the High Sulfur Exhaust Gas Condition

Marine diesel engine SCR systems usually use honeycomb or plate vanadium-based catalysts, and SCR reactions are a gas–solid heterogeneous reaction that occurs on the catalyst surface [72]. Generally, the SCR reaction process includes standard SCR reaction, fast SCR reaction, slow SCR reaction and its side reactions [73].

Standard SCR reaction:



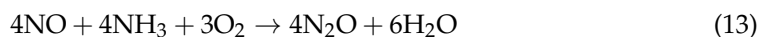
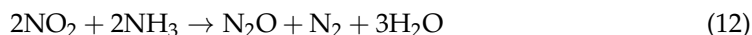
Fast SCR reaction:



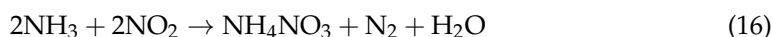
Slow SCR reaction:



When the exhaust gas temperature of the marine diesel engine is high, the by-product N_2O is generated, and part of NH_3 is oxidized in the SCR reaction. The related side reactions are:



When the exhaust gas temperature of the marine diesel engine is low, the catalyst will have some side reactions that will mainly include the formation reaction of ammonium salts such as sulfate and nitrate [74,75]. The related side reactions are:



Only when the reaction temperature is higher than $350\text{ }^\circ\text{C}$, reaction (14) and (15) may occur, and the reactions will be more violent when the temperature is higher than $450\text{ }^\circ\text{C}$. When the exhaust gas temperature of the marine diesel engine is lower than $250\text{ }^\circ\text{C}$ and contains a large amount of NO_2 , the reaction as shown in Equation (16) will occur [76].

The exhaust gas of diesel engine contains a large amount of NO due to the oxygen-rich combustion. Therefore, the denitration efficiency of the SCR system is mainly limited by the standard SCR reaction and the fast SCR reaction [77]. As the SCR side reactions occur under the harsh conditions and are relatively insignificant in magnitude, the effects of its side reactions are ignored [78]. Based on this characteristic, the denitration mechanism mainly depends on the standard SCR reaction and the fast SCR reaction, and it is believed that it follows the Eley–Rideal mechanism or the Langmuir–Hinshelwood mechanism [79–81]. The denitration reaction mechanism based on the standard SCR reaction path proposed by Topsoe laboratory is shown in Figure 9.

The study found that this reactor mechanism or model can predict the progress of SCR reactions in automotive SCR systems or marine LP-SCR systems, but the prediction accuracy is poor for low-speed marine diesel engines under high sulfur fuel and low temperature exhaust [82].

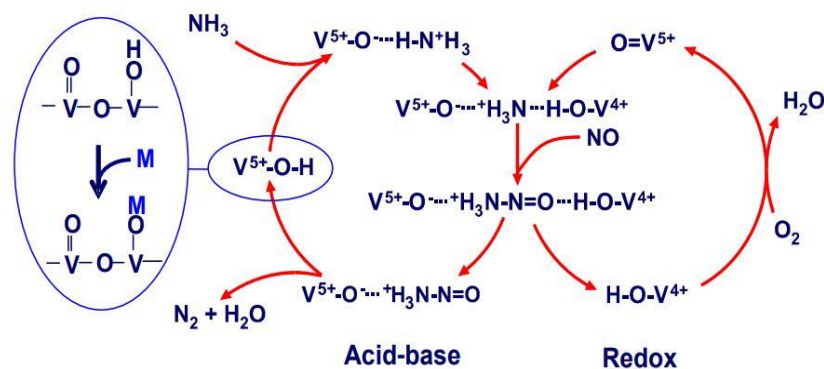


Figure 9. Denitration reaction mechanism based on standard SCR reaction path [52].

Considering that the marine diesel engine uses inferior fuel, the exhaust gas temperature is low (up to 200 °C or lower), and the SO_x concentration in the exhaust gas is higher (up to 700 ppm or higher) [83], so the operating temperature range of the SCR system will inevitably be within the acid dew point of the ammonium salt, and the products of sulfates and nitrates will limit its denitration performance. At present, the study of catalysts and catalytic mechanisms is less common under marine diesel engine exhaust conditions [84], but studies on heavy metal poisoning [85] and the sulfur poisoning [86,87] of catalyst samples have been ongoing under laboratory conditions. Therefore, catalyst sulfur poisoning or passivation can be divided into two types [88]: first, the gas-phase SO_x and the catalysts or the heavy metals in the exhaust gas form stable substances [89]; second, the gas-phase SO_x and NH_3 in the exhaust gas generate ammonium salt substances that are easily decomposed at high temperatures [90]. The difference is that the former is irreversible (catalyst deactivation) and the latter is reversible (active passivation).

These easily form sulfates and nitrates with NH_3 at low temperatures, because SO_x and NO_x are both acid gases [91]. In addition, the exhaust temperature of marine diesel engines is low and the composition of exhaust gas is complicated [92]. When there is a large amount of SO_x and H_2O in the exhaust gas, the formation reactions of ammonium salts will occur, and the ammonium salts will block the catalyst surface and pores [93,94] and greatly reduce the activity of marine SCR catalysts [95]. These ammonium salts mainly include ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulfate (NH_4HSO_4), ammonium sulfite ($(\text{NH}_4)_2\text{SO}_3$), ammonium bisulfite (NH_4HSO_3), ammonium nitrate (NH_4NO_3), etc. [96], and their properties are relatively unstable and easily decomposed at high temperatures. In other words, when such ammonium salts have formed, the catalyst activity can be restored after high temperature treatment. Therefore, such reactions can be called catalyst ammonium salt passivation reactions [97].

For sulfates, the acid dew point temperature of ammonium bisulfate is usually 280–320 °C, the formation of ammonium bisulfate limits the minimum operating temperature of the SCR catalysts [98,99]. When the temperature is lower than the acid dew point, ammonia gas and sulfuric acid vapor will condense into ammonium bisulfate and block the surface structure of the catalyst [100]. The reaction process is reversible, when the operating temperature rises above the dew point, the ammonium bisulfate will evaporate and the catalyst activity will be restored [101]. However, the catalyst activity will change permanently if the operating temperature is lower than its dew point for a long time, which means the catalyst will be deactivated [102]. At the same time, V_2O_5 in the vanadium-based catalyst will promote the oxidation of SO_2 to SO_3 in the exhaust gas (Figure 10), which will aggravate the formation of ammonium sulfate [103].

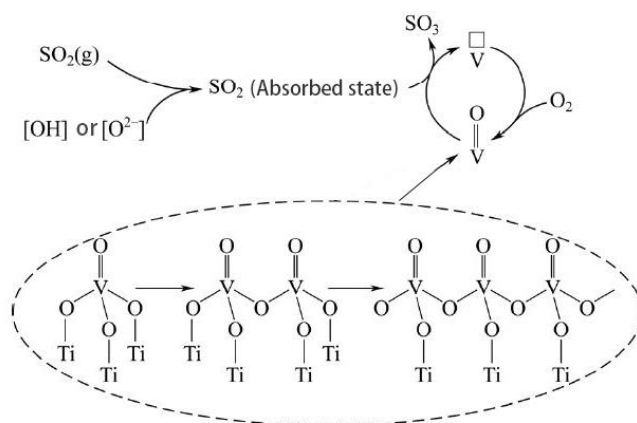


Figure 10. Mechanism of SO₂ oxidation on the surface of vanadium-based catalysts [92].

Different from ammonium sulfate, the effects of ammonium nitrate are mainly reflected in, first, inhibiting the formation of intermediate products (NH₄NO₂) in the fast SCR reaction path [104,105], and second, blocking the surface structure of the catalyst. Nevertheless, nitrate is easier to decompose than sulfate, and it can decompose at 170 °C [106]. Therefore, low temperature is an important reason for the formation of ammonium nitrate sediments.

5. Research on Engine Tuning and Control Strategy under Variable Operating Conditions

The exhaust gas states of marine low-speed diesel engines cannot directly meet the SCR working requirements due to the low temperature and complex composition of the exhaust gas [107], which strongly limits the denitration efficiency of the marine SCR systems [108]. The marine diesel SCR system, especially the two-stroke low-speed diesel SCR system [109], must rely on different engine tuning technologies to increase the temperature of its exhaust gas to obtain the higher denitration efficiency [110–112].

The engine tuning process of the low-speed diesel engine is shown in Figure 11. During its operation, the pneumatic valves are used to control whether the exhaust gas flows through the SCR reactor or whether the exhaust gas has been treated [113]. For the diesel engines that meet the IMO Tier II standard [114], the switch of the bypass valves determines the working mode of the diesel engine—Tier II mode or Tier III mode [115], and the two working modes of the diesel engine also meet different emission standards [116]. The marine diesel SCR system uses a discontinuous operation mode due to the differences of emission regulations in different sea areas [117]. The cold wall surface and the catalyst windward side are easily blocked by crystals under non-continuous operation conditions, which causes the consumption and waste of a large amount of reducing agent [118,119].

When the low-speed marine diesel engine burns the inferior high sulfur fuel, a large amount of gas-phase SO_x will inevitably exist in its exhaust gas [120]. In this case, it is necessary to confirm the minimum operating temperature of the SCR system or denitration catalyst to avoid the formation of sulfate and other deposits [121]. Generally, the operating temperature of the high-pressure SCR system is required to be higher than 320 °C to avoid the generation of sulfate and nitrate under the high sulfur exhaust gas conditions (fuel sulfur content 3.5%) [122,123]. For marine diesel engines, the exhaust gas temperature before the turbine can only meet this requirement under some operating conditions [124]. In particular, though the marine low-speed diesel engines have higher thermal efficiency, the exhaust gas temperature before the turbine is difficult to meet this requirement under most working conditions [125]. When the load of the diesel engine is below 15% MCR, the injection of urea solution must be stopped to prevent the formation of large amounts of deposits at low temperatures [126].

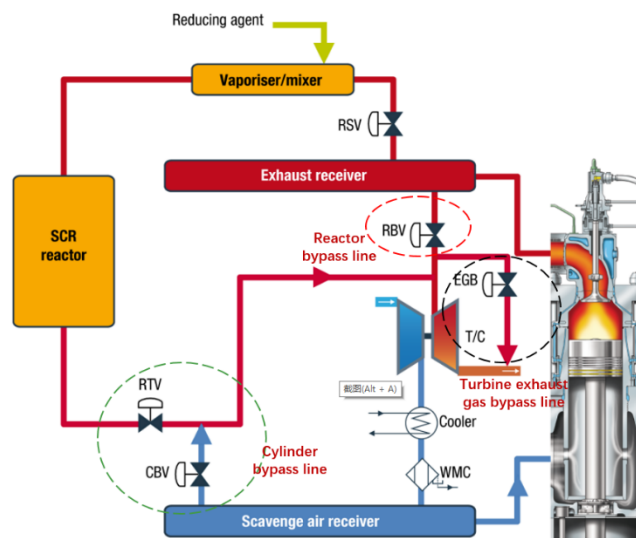


Figure 11. Flowchart of low-speed diesel engine main engine tuning method [18].

At present, the common engine tuning methods mainly include CBV and turbine EGB [127,128]. By reducing the quantity of the fresh air entering the combustion chamber and increasing the amount of fuel injected [129], the exhaust gas temperature is increased at the expense of the fuel economy [130]. Both technologies can increase the exhaust gas temperature, but it will decrease the main engine power output [131] and fuel economy [132], it will also bring the matching problems between the main engine and the turbine [133–135]. The change trends of exhaust gas temperature and pressure before the turbine during variable operating conditions are shown in Figure 12 [136].

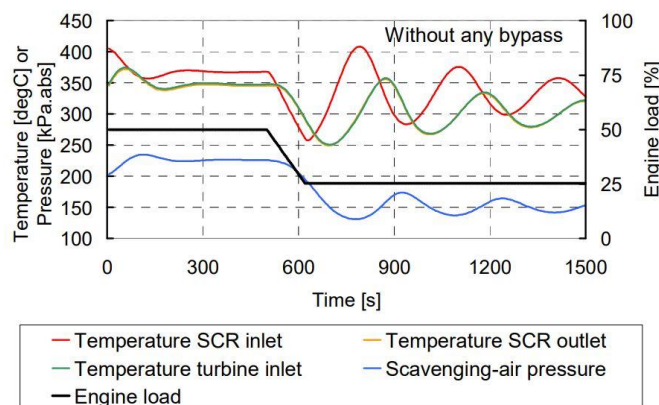


Figure 12. Matching situation between low-speed diesel engine and HP-SCR system under variable operating conditions [136].

In addition, when the operating conditions of the diesel engine change, there may be short-term differences or delays in the exhaust gas temperature before and after the reactor (between the exhaust gas header outlet and the turbine inlet) due to the thermal inertia of the SCR system catalyst [137]. It will cause the energy imbalance before and after the turbine and affect the normal operation of the turbine. Michael I. Foteinos et al. [138] showed the inlet and outlet temperature change of high-pressure SCR reactor during the main engine acceleration and deceleration, and the maximum temperature difference exceeds 100 °C. Of course, the degree and duration of the thermal delay mainly depends on the size of the SCR reactor and the heat capacity of the catalyst [139], but the low-speed diesel SCR system has a relatively large volume, and this thermal inertia has a greater impact on the transient performance [140].

6. Conclusions

(1) The HP-SCR system arranged in front of the turbine can make full use of the higher exhaust gas temperature and improve the catalyst activity. At the same time, the HP-SCR system has a higher working pressure, and its absolute pressure is much higher than that of the LP-SCR system, which is equivalent to reducing the volume flow rate or the linear velocity of the exhaust gas and increasing the SCR reaction time. Under the same design requirements, the HP-SCR system has the more compact structure and the higher energy efficiency, and it is more suitable for low-speed diesel engines with large power.

(2) The study of the SCR reaction mechanism under the limit conditions of high pressure and high sulfur is an important theoretical basis for solving the practical application problems of low-speed diesel engines. Low temperature is an important reason for the formation of ammonium nitrate, ammonium sulfate, and other deposits. Additionally, the formed deposits will directly affect the working performance of the SCR systems. The passivation mechanism of the ammonium salt under the high sulfur exhaust gas is an important basis for determining the operating requirements of the HP-SCR system. Additionally, the passivation mechanism of the ammonium salt must consider the effects of sulfate and nitrate comprehensively.

(3) To solve the problem of the practical application of the HP-SCR system, it is of great significance to construct the model for predicting the transient performance of the marine low-speed diesel HP-SCR system and study the engine tuning method or cooperative control strategy under variable operating conditions. Under the condition of low sulfur exhaust gas, the emission reduction effect of the SCR system can meet the Tier III requirements, while under the high sulfur emissions it struggles to meet the requirements of Tier III regulations. Therefore, when the low-speed diesel engines burn high sulfur heavy oil, it is necessary to take relevant engine tuning measures.

(4) At present, SCR technology is the most mature and effective technology to deal with nitrogen oxide emissions and has been widely used in the shipbuilding industry. In the future, the emission standards of nitrogen oxides will become more and more stringent, and it is of great significance to study more efficient denitration technologies. At the same time, due to the development of marine energy-saving technologies, the thermal efficiency of low-speed diesel engine is continuously improved, which makes its exhaust temperature drop constantly. Under the dual restrictions of high sulfur fuel and low exhaust temperature, the low-speed diesel engine SCR systems will inevitably sacrifice part of the engine economy to obtain higher denitrification efficiency and operational reliability. For HP-SCR products, it will develop in the direction of miniaturization, integration, and high efficiency, and may be integrated on the engine in future development. For LP-SCR products, it will focus on low-temperature catalyst research and urea decomposition efficiency to improve the denitration efficiency and service life of the LP-SCR system.

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Abbreviations

CBV	Cylinder Bypass Valve
CO	Carbon monoxide
CO ₂	Carbon dioxide
DEF	Diesel Exhaust Fluid
DPF	Diesel Particulate Filter
ECA	Emission Control Areas
EGB	Exhaust Gas Bypass Valve
EGR	Exhaust Gas Recirculation
HCS	Hydrocarbons
HFO	Heavy Fuel Oil
HP-SCR	High-Pressure SCR
H ₂ SO ₄	Sulfuric acid vapor
IFO	Intermediate Fuel Oil
IMO	International Maritime Organization
LP-SCR	Low-Pressure SCR
MCR	Maximum Continuous Rating
MDO	Marine Diesel Oil
NH ₃	Ammonia
NH ₄ HSO ₃	Ammonium bisulfite
NH ₄ HSO ₄	Ammonium bisulfate
NH ₄ NO ₃	Ammonium nitrate
(NH ₄) ₂ SO ₃	Ammonium sulfite
(NH ₄) ₂ SO ₄	Ammonium sulfate
NO _x	Nitrogen Oxides
PM	Particulate Matter
RBV	Reactor Bypass Valve
RO	Residual Oil
RSV	Reactor Sealing Valve
RTV	Reactor Throttle Valve
SCR	Selective Catalytic Reduction
SO ₂	Sulfur dioxide
SO _x	Sulphur Oxides
UFP	Ultrafine Particles
UWS	Urea-Water Solution
VOC	Volatile Organic Compounds

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