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SOME METHODS OF REDUCING NO_x COMPONENTS IN EXHAUST GAS

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ABSTRACT

NOx nitrogen emissions arise through the burning of fuels at high temperatures, through chemical processes that use nitrogen. In nature, from the nitrogen oxidation of the air due to lightning, volcanic gas and microbial decomposition processes. Nitrous oxides normally exist in the air at very small concentrations and do not cause pollution concerns. However, along with the development of transportation, vehicles that emit NO_x emissions beyond the permitted levels are seriously affecting the air quality. This article presents some solutions to absorb or convert NO_x in waste gases to reduce environmental pollution.

Keywords: formation mechanism, emission, nitrous oxides, solution.

1. INTRODUCTION

With a history of developing for hundreds of years, the engine industry has grown and achieved extraordinary milestones. In recent years, the design and development of internal combustion engines have not only focused on operational and economic performance but also on environmental issues. The engines in general and diesel engines in particular are one of the most polluting sources in our country, especially in urban areas. Along with the growth of the economy, the demand for means of transport used in the fields of trucking, aviation and shipping has increased. In order to meet the demand for public transportation services, the number of buses also increased. However, the number of buses meeting Euro II in Vietnam emission standards is still very low. In order to limit these polluting components, many solutions have been proposed including solutions with engines and emission control solutions. Measures to reduce emissions for diesel engines mounted on buses in particular and vehicles are generally one of the most urgent issues.

Today sustainable development is always concerned about every country in the world, especially the protection of the human environment. The human environment is severely damaged by various sources and one of the major sources of pollution is internal combustion engine emissions - which provide up to 80% of the world's energy consumption. Internal combustion engines are a type of heat engine, because the combustion of fuel, the process of switching from the heat of the gas to the engine is carried out right in the engine charcoal. The reciprocating internal combustion engine has high thermal efficiency because the maximum temperature in the combustion process can be up to 1800K-2800K, while the exhaust gas temperature is about 900-1500K. Especially turbocharged turbochargers are the most efficient in all types of engine engines today. The detailed consideration of the negative impact of internal combustion engines is of paramount importance and the aspects to be considered are: Evaporation pollution of fuel. Pollution due to exhaust gases, pollution by chatting and fuel additives, reduced visibility due to smoke and unpleasant odors of diesel exhaust. As we know, in the world today there are approximately 1 billion cars, annually emitting millions of tons of toxic environment. Particularly in Vietnam, along with the socio-economic development, speed increases. Every year the above mentioned means is quite high. For example, the average motorcycle growth rate of 2015 is 12.48%. At 31.12.2016, the country had 460.000 cars and 5.585.000 motorbikes. At present, the majority of motorbikes are concentrated in big urban areas such as Hanoi and Ho Chi Minh City, causing extreme environmental pollution [2]. Therefore, research to limit engine pollution emissions is an urgent requirement for any country.

Thus, it can be seen that in order to reduce the pollution by exhaust gas in a comprehensive and effective manner, it has to synchronously conduct a series of complex tasks, from research, design, fabrication to operation. Facilitate and research, develop and implement standards for specific audiences. Emissions from engines in general and diesel engines in particular account for a significant share of total emissions. Diesel emissions include carbon dioxide (CO_2), water vapor (H_2O), nitrogen (N_2), and oxygen (O_2); Carbon monoxide (CO), hydrocarbon (HC), nitrogen oxides (NO_x) and particulate matter emissions (PM). Of these components, the first four emitters accounted for 99%; The next four emissions groups account for only 1%, but they have a great impact on human health as well as on environmental pollution [2]. Therefore, the issue of reducing

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emissions of engines in general and diesel engines in particular is of the world interest, research to provide solutions to reduce emissions. NO_x content in diesel engine emissions is quite small. NO_x consists of nitric oxide (NO) and nitrogen dioxide (NO_2). NO_2 is more toxic than NO, which has a direct effect on health and is a source of ozone formation as well as a major cause of fog formation [4, 5]. It is born in the combustion process due to the chemical reaction between the oxygen and nitrogen atoms. The reactions that make up NO_x are highly dependent on temperature. Therefore, the amount of NO_x discharged from the engine is usually proportional to the load of the engine [3]. Using exhaust gas discharge is an effective way to reduce NO_x emissions.

2. NO_X FORMATION MECHANISM

It is difficult to understand the mechanism of NO_x formation in diesel engines and to control the emission of this exhaust gas because of the rapid combustion of diesel engines and the combustion mixture is not uniform. NO, NO_2 are the two major components of NO_x. In it, NO is colorless odorless gas while NO_2 is reddish brown and has a strong odor. Both gases are very toxic but NO_2 is 5 times more toxic than NO, the majority of NO_2 is formed by NO oxidation. NO is formed during the combustion failure in the cylinder at high temperatures, the mechanism of NO formation widely accepted is the mechanism introduced by Zendovich. The main ingredient for NO formation is N_2 gas in the air loaded into the engine. The nitrogen gas oxidation reaction is made up of oxygen atoms, formed by the separation of the O_2 molecules at high temperatures during combustion.
The main reaction for the formation of NO from N_2 is:

$$O_2 \rightarrow 2O$$

$$N_2 + O \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

$$N + OH \rightarrow NO + H$$

These equilibrium equations indicate that combustible gases at normal combustion temperatures have a very small NO_2/NO ratio. Meanwhile experiments on gasoline or diesel engines show that NO_2 can account for 10% to 30% of NO_x. This is explained by the fact that NO formed in the flame zone can quickly become NO_2 by reaction:

$$NO + H_2O \rightarrow NO_2 + OH$$

Next, NO_2 reacts and becomes NO by reaction:

$$NO_2 + O \rightarrow NO + O_2$$

Otherwise NO_2 formation in the hot flames area will be extinguished when exposed to cold areas. Hence, the NO_2/NO ratio will be highest at the high load mode of the diesel engine, where cold zones can suppress the formation of NO. The local concentration of oxygen atoms depends on the concentration of the oxygen molecules as well as the local temperature. NO_x formation exists primarily at temperatures above 2000K. Therefore, any technique that can control instantaneous temperatures in the combustion chamber below 2000K can reduce the formation of NO_x. NO_x is formed from the oxidation of nitrogen under high temperature conditions of combustion. The NO_x composition is highly dependent on the air-to-air ratio (ie, the oxygen concentration of the mixture) and the temperature of the combustion. Here, the temperature of the combustion process is large enough for oxygen and nitrogen to decompose into highly activated atoms, where the oxygen concentration is high enough to provide enough oxygen for the reaction, so the NO_x reaches the maximum.
Due to the characteristics of the diesel engine that forms the internal mix, the air-to-air ratio is within a very wide range, namely 1.2 to 10, respectively, from full load to no-load. In diesel engines, when □ increases, the burning temperature decreases, so the NO_x content decreases. Compared to gasoline engines, diesel engines have lower NO_x content. However, the NO_2 content in NO_x is higher, accounting for the same proportion as the gasoline engine. The method of forming the mixture has a great influence on the formation of NO_x. For separate combustion chambers, the combustion takes place in the secondary combustion chamber (air

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restriction), which is deficient in oxygen, so although the temperature is high, NO_x remains small. When burning in the main combustion chamber, although λ is very large and much oxygen but the temperature of combustion process is not big, so NO_x is also small. In summary, the NO_x of the engine has a combustion chamber that is only about half that of a combustion engine. However, the engine using the combustion chamber is not economical because of high fuel consumption so it is not used much today.

3. EFFECTS OF NO_X

The impact of NO_x on human health: On average, people need 12m of clean air to carry out the metabolism and supply oxygen to the body. In the NO_x family NO_2 is the most toxic. However, in a caveat, NO can also be converted to NO2, so strict control of NO is required. NO_2 is a soluble substance, so it can travel through the airways to the lungs, causing pneumonia and damaging the cells of the alveoli. When entering the lungs, 80% of NO_2 is trapped. Patients suffer from insomnia, cough, shortness of breath. In addition, NO_2 can cause damage to the eyes and stomach. $[NO_x]$ = 0.005mg/l (air). If the NO_2 concentration exceeds 100ppm, humans and animals can die within minutes of exposure.

First of all, the presence of pollutants in the air affects the hydrocarbon balance that forms the photocatalytic layer that causes tropospheric O_3, One of the components pollutes the environment. However, it is a necessary substance in the stratosphere to filter ultraviolet rays (a type of ray that is very harmful to the skin, which can cause skin cancer).
Meanwhile, N_2O is a gas that can damage the ozone layer. On the other hand, NO_2 also reacts with H_2O to form acid by reacting:

$$NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The acids dissolve in rain, snow, fog and are more severe than HNO_3 levels. Enormous amounts of acid can cause acid rain that damages the vegetation and corrodes the structure.

Effect of NO_x on plants: When NO_x concentration in the air is greater than 0.5-0.7ppm, it reduces photosynthesis in plants. In high urbanized areas, when NO_x reaches about 3.93ppm. This is a matter of concern, because photosynthesis is the process of re-supplying oxygen to the air.

4. SOLUTIONS FOR REDUCING NO_X EMISSIONS

Since the issue of environmental pollution due to engine exhaust has begun to be taken care of, researchers have focused their efforts on limiting the emission of toxic substances from the engine. Pollution of exhaust gas can be divided into two main groups:

The first group: Including measures related to engine structure, mixture method ... to reduce pollution at the base.

The second group: Including exhaust gas treatment measures to ensure that the concentration of toxic substances in the exhaust gas into the environment must be less than the limit allowed.

CDC engine
The clean diesel engine design (CDC) method revolves around a series of traditional diesel engine design modifications to reduce NO_x emissions, maintain the advantages and improve efficiency of diesel engines. The essence of CDC technology is the development of the NO_x-producing ability of the combustion engine. The amount of NO_x produced is significantly reduced in the combustion chamber of the engine but does not affect the efficiency of the engine. Early EPA studies demonstrated that with the new design of the diesel engine, the amount of NO_x produced inside the cylinder was significantly lower than the industry average. Solutions used in CDC technology:

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Use hydraulic booster fuel system to reduce black soot and reduce the amount of smoke generated, increasing the efficiency of the engine.

Booster system: Increases engine power and increases the efficiency of combustion, thus reducing the amount of combustion gases and increasing fuel economy.

Low pressure exhaust: Maximum temperature is the main cause of NO_x formation during combustion of diesel engine, so the formation of NO_x gas decreases if the temperature of the combustion chamber is reduced.

Carbon black has been treated: reducing the amount of excess smoke and the amount of hydrogen-carbon (HC) does not burn out, the carbon dioxide in the exhaust gas is reduced, so standard compliance in the future.

The challenges facing this technology are the reduction of the emission of direct emissions from the engine, demonstrating the practical application of this technology in world practice, keeping the value, the level of Sustainable, step by step approach to strict standards for emissions of developed countries.

Exhaust gas recovery system

When the temperature in the engine combustion chamber is too high due to the compression ratio of the engine, nitrogen gas in the air combined with oxygen will form nitrogen oxides (NO_x). This is one of the components causing environmental pollution. Therefore, the best way to reduce NO_x is to reduce the combustion chamber temperature and reduce the O_2 content.

To achieve this, the best solution is to use Exhaust Gas Recycling (EGR). The essence of this measure is to put some of the waste back into the combustion chamber. The EGR system can be used for both gasoline and diesel engines.

On gasoline engines: EGR is a commonly used measure. Combustion gases consisting of HC, CO, NO_x with high temperature after exiting the combustion chamber are extracted partially back to the combustion chamber for the next cycle of the engine. This increases the air temperature at the end of the compression stroke, ensuring the temperature conditions for the fuel mixture to be burned easily.

The application of ancillary systems combined with a basic emission treatment solution will help automobile manufacturers meet the stringent emission standards in the world.

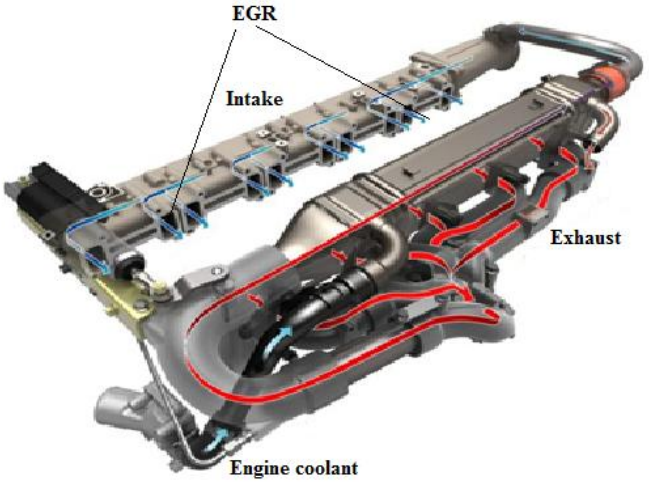

Figure 1. Principle diagram of exhaust gas recovery system

However, because the gas mixture occupies a certain volume in the combustion chamber, the maximum temperature of the combustion process is lower than that of the non-EGR system, thus reducing the NO_x concentration. Two types of exhaust gas can be used:

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+ Inner Circulation: The method is based on the same angle of the loading coil and the coil (both open). During the phase of the message, due to the pressure difference (the pressure is greater than the air pressure), the exhaust gas in the cylinder enters the intake manifold and then returns to the cylinder during the load. This measure not only reduces the NO_x but also reduces the amount of unburned carbon (HC) hydrocarbons as the HCs circulate back into the combustion chamber before loading the new mixture.

+ External Circulation: Exhaust emissions will be extracted from the waste stream back to the feeder to be blended with the new air intake through the EGR feeder and control valve system. The EGR valve is controlled by an electronic controller that operates on two input signals, the motor speed and the motor load.

However, besides these advantages, the EGR system will contaminate the intake manifold, reduce fuel economy and make the engine unable to reach peak power at full load. Therefore, the EGR system usually operates in a small load mode. In addition, in idle mode, the recirculation of the exhaust gas makes it easy for the engine to die (due to too poor combustion mixture).

On diesel engines: the rate of circulating exhaust gas can be higher than the gasoline engine (direct injection diesel has 60% renewable exhaust gas, indirect injection diesel engine about 30%). But the use of EGRs on diesel engines also reduced fuel economy, increased HC and solid PM (PM-carbon footprint) emissions, and the engine was unstable, affecting power.

In fact, the EGR system on diesel engines is much more complex than the gasoline engine due to the low vacuum on the feeder (low speed rpm). Therefore, in addition to the electronic control unit, pneumatic valve, exhaust gas valve, the system also has to add a vacuum pump.

Similar to gasoline engines, diesel engines can also utilize internal exhaust gas circulation to reduce NOx and HC. Currently, there are many diesel engines on the car that use small amounts of exhaust gas at several operating modes (low speed and low load). In the future, this system will be more commonly used to meet increasingly stringent emission regulations.

Waste heat treatment system

The principle of this system is to keep the waste gas for a long period of time at high temperatures, in order to prolong the oxidation of the CO and HC components. For efficient heat treatment, the heat treatment reactors are located immediately after the waste coil, ensuring a reaction temperature of T > 1.000K for oxidation. Reaction enclosures are insulated and sized to accommodate large amounts of exhaust.

In working mode with a small air residue ratio, part of the air will be added through a pipe just after the downstream pulse. Heat treatment systems are very efficient with engines that work with rich mixtures. However, the heat treatment system does not reduce the amount of NO_x.

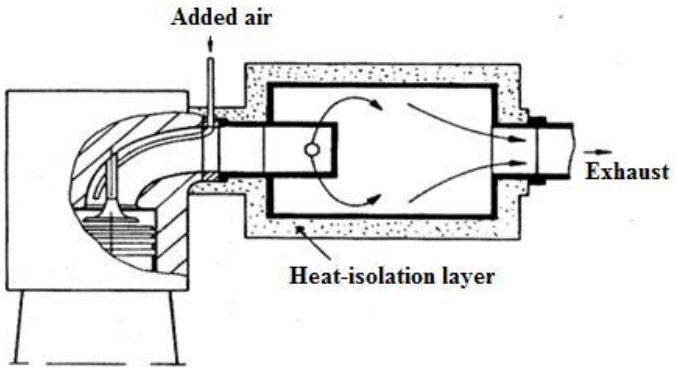

Figure 2. Principle diagram of waste heat treatment system

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Use a neutral gas catalyst

Non-catalysts using SNCR only use urea or NH_3 without catalyst so the cost is low. The reactions occur in certain temperature ranges and the high temperature range for SNCR operation is very narrow, the optimum temperature for effective SNCR is about $900 \div 1100^0$C so it should be applied to the exhaust stream having high temperature, stable operation and reasonable SNCR regulator.

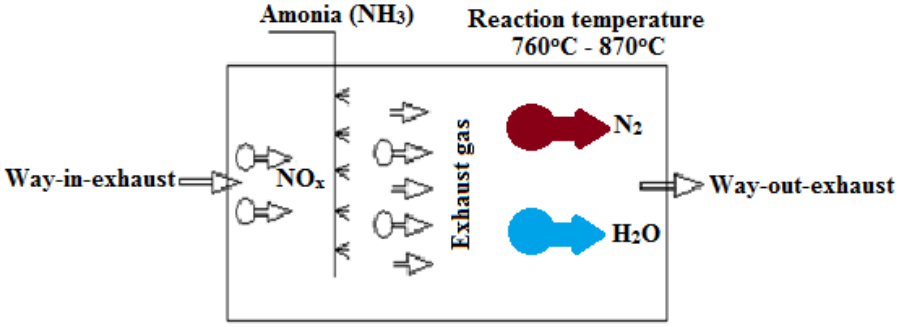

Figure 3. Principle diagram of SNCR

The advantage of this type is the low cost, easy to install but operate in the narrow temperature range. The reactions are the same as the SCR but only at the right temperature range, so the range of activity of SNCR is very narrow, the reduction in NO_x efficiency is lower than the SCR but the price is much cheaper because it is not. Equipped with catalysts. The SNCR system reduces 30-60% of NO_x, minimizes the operation of the machine, easy to install, the fact that SNCR is less used than SCR, SNCR mainly applies to boilers where the agent is sprayed directly into Boiler chamber at very high temperature in accordance with SNCR reaction.

Chemical methods have the advantage that they can be applied to older engines without affecting the structure of the engine, the engine only needs to be equipped with this device in the exhaust line. But the process has not been completed because either NO_x or NH_3 (Ure) is redundant, resulting in difficulty adjusting the flow. Some NH_3 slides out of the catalyst and high temperature NH3 is no longer neutral but oxidized to pollutants, and NH_3 is very toxic, so it should be reasonable, temperature range Appropriate, now tend to use urea due to safety, less toxic.

5. APPLIED SOLUTION FOR MARINE DIESEL ENGINE

As mentioned and analyzed in part two, there are many measures to reduce pollution. The solution may include an engine action to reduce NO_x emissions from combustion, post-combustion treatment or the selection of fuel and fuel mixture. Efficiency, complexity, applicability and cost are different. Moreover, the choice of methods must be appropriate to the actual conditions of our country. The method of finishing the structure of the combustion chamber and the nozzle is interested and concerned manufacturers to build engine. At present, the new engines produce major improvements in structure and ensure NO_x emission standards. Our country is mainly old engines that need to overcome the NO_x emissions, so the work on the structure, related to fabrication is unreasonable and difficult to implement.

Adjustment of the regulator parameters also has the effect of minimizing the pollution but the efficiency is not high due to the old engine condition, some of the servicing equipment are not suitable for increasing the injection pressure, reducing the delay. However, this adjustment also needs to be made in engine repairs to reduce NO emissions due to poor engine technology. The direct injection of water or NH_3 into the combustion chamber significantly reduces NO_x formation in the engine but it is difficult to touch the engine's structure due to the addition of a nozzle positioned on the cylinder cover. Engine, this is very difficult, especially when the number of cylinders is high, the greater the complexity.The use of fuel-oil emulsion mixtures is better, but the fuel system needs improvement, the equipment for the complex mixing process and the blending ratio is very small, not applicable to the engine using heavy diesel fuel. In fact, the world applies only to small-duty diesel engines using light fuel, for example in Germany, which applies to some passenger cars that have not yet been applied to large-duty Diesel engines such as ship diesel engines. The exhaust gas has a significant reduction in

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NO_x, the structure of the engine changes little, it is inexpensive but the return rate is limited due to the engine power, the PM particle emissions, especially Low speed motors have a great impact on the quality of lubricating oils, abrasives, and engine life. Therefore, it is possible to select this method but it should be combined with other measures to achieve the NO_x emission standard without compromising on engine power and lifetime.

Neutral adsorption neutralizing devices have a very high NO_x reduction effect, in addition to reducing emissions of substances such as CO and HC. This method is mainly applied to gasoline or diesel engines with small capacity of soot and sulfur. Some manufacturers develop this type of adsorption neutralization device to apply to cars, passenger cars using light fuel. With large diesel engines due to the large amount of soot affect the absorption and economics of the device. The chemical method of using neutralizing gas is widely applied in the world and many manufacturers have applied to marine engines and achieved good performance, high equipment life, can Over 10 years. Chemical methods using neutralizing chemicals are two types of SCR and SNCR are non-catalytic, inexpensive, but not very effective, operating in a narrow temperature range and very high, it is combined with high speed cruise speed diesel engines. Neutralizing devices with neutralizing agents such as NH_3, urea using a catalyst (SCR) reduce to 80 ÷ 95% of NO_x in the exhaust gas, when fitted to the engine it replaces the sound absorbed so negatively. What up to the engine room space. No major impact on the structure of the engine but just add to the exhaust pipe. This method can be applied to old diesel engines in our country. However, in the exhaust gas there is also a small fraction of S and soot makes the neutralization with NO ineffective so it may be required to use a low S-content fuel, which can be overcome by Annex VI Marpol 73/78 also requires SO_x emissions, where the main measure to reduce SO_x is the use of low S-content fuel, which controls NO_x emissions right from the start as fuel control. The engines that apply the standard of the Annex must simultaneously carry out two of these, reducing the emission of NO_x and SO_x, ie, to take measures on the engine structure or neutralization of the exhaust. To reduce NO_x emissions and use less S fuel to reduce SO_x. So with the old marine diesel engines like in Vietnam today, the method of neutralizing exhaust gas with SCR neutralizers is proposed. The SCR system in ship is easy to deploy on board without compromising engine room space, not to the engine or engine chamber. Catalytic converters replace the engine's noise gates. The system includes a urea solution, pump, control system and nozzle. The electronic control system is responsible for detecting the NO_x content in the exhaust gas after the catalytic converter is removed and compared to the allowable value. From there, it gives control signals to the urea flow control devices such as nozzles and pumps to match the NO_x concentration. For turbocharged engines, the system is positioned ahead of the turbocharged turbocharged, ie, the exhaust after neutralization enters the turbine.

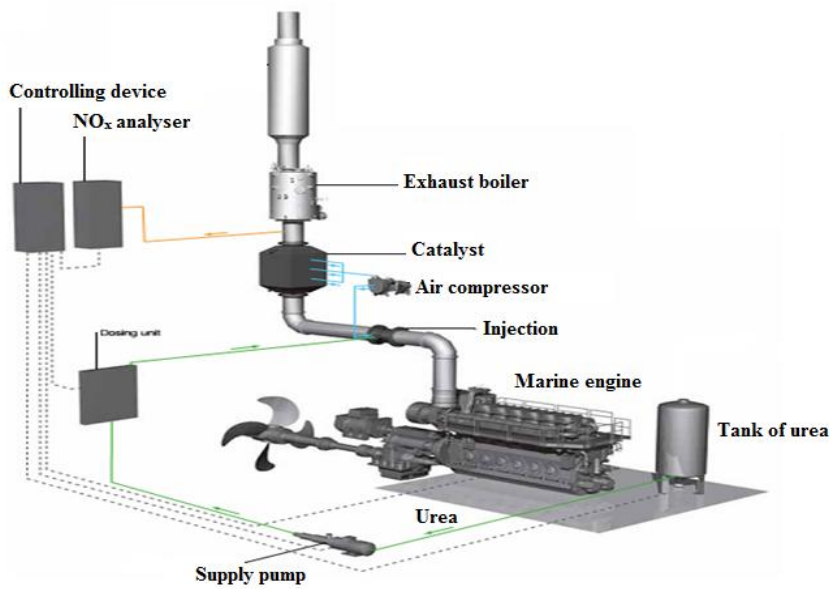

Figure 4. Principle diagram of SCR on ship

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6. CONCLUSION

For older internal combustion engines such as those in Vietnam, small and medium-sized engines can choose to discharge exhaust gas, heat treatment or filter inserts. For large-capacity engines, you may choose to neutralize exhaust gas with SCR-based neutralizers or use biodiesel fuel and SCR systems at the same time. SCR-based neutralizing devices reduce the NOx emissions to 80 to 95% in the exhaust gas, which, when fitted to the engine, replaces the negative electrode so that it does not affect the chamber space. No major impact on the structure of the engine but just add to the exhaust pipe. This method can be applied to old diesel engines in our country. Using SCR is the direction in which the world has come to use and there have been many manufacturers of controllers and catalysts with simple principles that can be widely applied to a large range of marine diesel engines. However, the use of an expensive SCR system is a must, as a catalytic reaction system and a urea tank, as well as equipment such as blending, spraying, etc. Although urea prices are relatively low, urea supplies are ubiquitous, as it is a common commodity. But the accompanying cost of operation, which is the largest cost, is mainly related to the handling of the urea mass contained on the vessel, which costs about 4-6 Euros per MW.h. Solution of using SCR systems are relatively expensive. Priority should be given to SCRs with high initial NOx emissions, high powered engines, and multi-engine based on ships will reduce NOx emissions. Application of SCR needs to fabricate the catalyst, select the temperature range suitable for internal combustion exhaust gas temperature, use NOx concentration control system.

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