Desulfurization and Denitrification of Ship Exhaust Gas with Low Temperature Plasma

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Abstract. In order to reduce the emission of pollutants such as sulfur oxides and nitrogen oxides in ship exhaust gas, the principles and experimental methods of desulfurization and denitrification with low temperature plasma with dielectric barrier discharge were introduced in this study. The impacts of reactor voltage and reactor frequency of low temperature plasma, humidity and oxygen content of ship exhaust gas on the efficacy of desulfurization and denitrification were also explored by experiments in this study. It was revealed that the low temperature plasma technology could desulfurize and denitrify the ship exhaust gas better. The efficacy of desulfurization and denitrification would be increased when the voltage increases. At a voltage of 20 kV, the removal rates of NO and SO\(_2\) reached 59% and 52% respectively. When the reactor voltage was maintained at 15 kV, the removal rates of NO and SO\(_2\) would rise at the beginning and decrease later with increase of the frequency. The highest removal rates of NO and SO\(_2\) were 55% and 42% respectively when the frequency was 10 kHz. The efficacy of desulfurization and denitrification can be affected by humidity and oxygen content of the ship exhaust gas. Researches in this study provided a crucial reference for the application of low temperature plasma technology in the desulfurization and denitrification of ship exhaust gas.

Keywords: dielectric barrier discharge; low temperature plasma; exhaust gas treatment; desulfurization and denitrification.

1. Introduction
With development of economic integration and trade globalization, advantages of ship transportation in terms of safety, transportation volume, and price become apparent increasingly, and induced pollution in various categories develops rapidly. Among them, the air pollution caused by ship exhaust gas occupies a large proportion. The ships are equipped with diesel engines, which can generate plenty of sulfur oxides and nitrogen oxides after combustion. It will result in serious air pollution if the exhaust gas of the ship is discharged without proper treatment [1]. In order to reduce the emission of pollutants such as sulfur oxides and nitrogen oxides in the ship exhaust gas, the ship exhaust gas has to be desulfurized and denitrified. The traditional treatment of ship exhaust gas is to desulfurize and denitrify separately. In this way, the efficacy of desulfurization and denitrification is high, but it will waste a lot of cost, and the operation is more complicated [2].
In recent years, there are a large number of researches on combined desulfurization and denitrification in China and overseas. Some scholars have proposed to take NaOH solution as an absorbent to desulfurize and denitrate, but the requirement for the absorbent is too high, and the absorption effect is not so good [3]. Some scholars have proposed to use the activated carbon adsorption for desulfurization and denitrification. The process is relatively simple, the investment is less relatively, but the rate is too slow [4]. Some scholars have applied microorganisms for desulfurization and denitrification, and the effect is very good, but the investment is high, so is the requirement for the environment [5]. Recently, some scholars have used the plasma generated by the electron beam radiation method and the pulse corona method for desulfurization and denitrification, but the operation cost is expensive, and the technical content of the operation is high relatively [6]. Thus, combined desulfurization and denitrification, as a key technology in the treatment of ship exhaust gas, have been concerned widely all the time.

In conclusion, a method of desulfurization and denitrification with low temperature plasma by using the dielectric barrier discharge is proposed in this study. Impacts of such method on efficacy of desulfurization and denitrification from the reactor voltage of low temperature plasma, humidity and oxygen content of the ship exhaust gas are explored in this study. Investigations in this study provide an important reference for application of low temperature plasma technology in ship exhaust treatment.

2. Methodology

Plasma is a system formed by various particles such as atoms, ions, free radicals, molecules, and electrons. The density of positive charge is exactly the same with that of the negative charge, the entire system is electrically neutral and is regarded as the fourth state of matter other than gas, liquid, and solid. In the universe, matter mostly exists in such state. Plasma was first discovered in 1879, but it was not introduced into the field of physics until 1928. Based on different apparent temperatures of plasma, it can be categorized as the high temperature plasma and low temperature plasma. The apparent temperature of high temperature plasma can be as high as 109K, and thermodynamic balance among the electrons, ions, and neutral particles is reached. The apparent temperature of the low temperature plasma is between 102K and 103K in common, but the temperature of electron is above 104K. In the system of low temperature plasma, most ions and neutral particles have different thermodynamic characteristics with electrons, and a large number of high-energy electrons and free radicals are in an excited state, which can provide enough energy for chemical reactions.

The plasma generated by the dielectric barrier discharge is a non-thermal and non-equilibrium plasma that can be generated at standard atmospheric pressure. The active electrons of such plasma obtained at low temperatures are just what needed for some complicated chemical reactions. Generation of low temperature plasma with dielectric barrier discharge can be affected by various factors, such as the distance between electrodes, the material of the insulating medium, the voltage, and the composition of the working gas. These years, the plasma with dielectric barrier discharge has revealed its unique application value in various fields, which has attracted more and more attention. The dielectric barrier discharge can generate the low temperature plasma with huge energy and concentrated density in a large space, so that a large amount of gas can take the chemical reactions of the plasma. Thus, the plasma with dielectric barrier discharge can be applied in the field of environmental pollution treatment in a wide range.

When the dielectric barrier discharge is used to generate the low temperature plasma, the working gas has to be filled fully between the two discharging electrodes, and the insulating medium used to block the discharge is fixed on the electrode, either one or both electrodes; or the insulating medium is placed between the two electrodes or is made into fine particles to fill the gap between the two electrodes. Thus, the two electrodes are applied with certain voltage to form an electric field, so that micro-discharge appears on the surface of insulating medium. In such way, the working gas can be broken down, and the gas starts to discharge, thereby generating the low temperature plasmas.

NO and SO2 are the major components of the pollutants in ship exhaust. When desulfurization and denitrification are performed by low temperature plasma generated by the dielectric barrier discharge,
chemical bonds of these molecules are broken to undergo ionizations and cracking reactions, forming the atoms, ions, and free radicals in initial state. That is these initial state atoms, ions, and free radicals react under the action of an electric field to achieve the purpose of desulfurization and denitrification. The experiment in this study is to fill the ship exhaust gas into the low temperature plasma reactor at a rate of 2 L/min under normal temperature and pressure for treatment, and the flue gas analyser is used to measure the concentrations of NO and SO\textsubscript{2} at the inlet and outlet of the low temperature plasma reactor. Thus, the removal rate of NO and SO\textsubscript{2} by the low temperature plasma technology of dielectric barrier discharge is calculated. The calculation method is as follows.

\[
\rho = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%
\]  

(1)

In equation (1), \( \rho \) represents the removal rate; \( C_{\text{in}} \) represents the concentration in inlet; and \( C_{\text{out}} \) represents the concentration in outlet. Experiments in this study explore the impacts of the voltage and frequency of the low temperature plasma reactor, the humidity and oxygen content of the ship exhaust gas on the removal rate of NO and SO\textsubscript{2}.

3. Results and Discussions

3.1. Impacts of voltage on desulfurization and denitrification

With several experiments, the average value is obtained in this study to investigate the relationship between the voltage in two terminals of the low temperature plasma reactor and the efficacy of desulfurization and denitrification.

![Figure 1. Relationship between voltage in two terminals of the reactor and the removal rate of NO and SO\textsubscript{2}](image)

The relationship between the voltage in two terminals of the low temperature plasma reactor and the removal rate of NO and SO\textsubscript{2} is shown in Figure 1. The removal rate of NO and SO\textsubscript{2} will become higher with increase of the voltage in two terminals of the reactor. At a voltage of 20 kV, the removal rates of NO and SO\textsubscript{2} reaches 59\% and 52\% respectively. It is because that when the voltage in two terminals of the reactor increases, the electric field strength will be enhanced, thereby the number of high-energy electrons and the density of active radicals in the reactor are improved. Removal NO and SO\textsubscript{2} by the dielectric barrier discharge technology mainly relies on the oxidation reaction between high-energy electrons and active radicals in the generated low temperature plasma. Thereby, increase of voltage can
improve the removal rate of NO and SO\textsubscript{2}. It suggests that the low temperature plasma with dielectric barrier discharge proposed in this study can realize positive desulfurization and denitrification on ship exhaust gas.

3.2. Impacts of frequency on desulfurization and denitrification

Several experiments were performed when the voltage in two terminals of the low temperature plasma reactor is maintained at 15 kV, focusing on the impacts of frequency of the low temperature plasma reactor on the efficacy of desulfurization and denitrification.

Table 1. Removal rate of NO and SO\textsubscript{2} at various frequencies of the reactor

| Frequency of reactor / kHz | Removal rate of NO / % | Removal rate of SO\textsubscript{2} / % |
|---------------------------|------------------------|---------------------------------------|
| 5                         | 10                     | 7                                     |
| 6                         | 15                     | 16                                    |
| 7                         | 30                     | 25                                    |
| 8                         | 39                     | 31                                    |
| 9                         | 49                     | 39                                    |
| 10                        | 55                     | 42                                    |
| 11                        | 47                     | 40                                    |
| 12                        | 38                     | 39                                    |

The removal rates of NO and SO\textsubscript{2} under various frequencies of reactor are shown in Table 1. It can be seen that the removal rates of NO and SO\textsubscript{2} increase at the beginning and decrease later as the frequency of the reactor increases continually. The highest removal rates of NO and SO\textsubscript{2} were 55% and 42% respectively when the frequency was 10 kHz. It is because that the amplitude of the active particles in the electric field will decrease as the reactor frequency increases under the condition of constant voltage. Increasing the frequency will provide more energy for the plasma reaction system during the discharge of the power supply, increasing the repetition rate of the discharge. With increase of the frequency, the number of high-energy electrons and active particles in the low temperature plasma reactor will increase, making it easier for the free radicals generated by the ionization of pollutant molecules to re-react and combine. Thus, the removal rate of NO and SO\textsubscript{2} will increase. When the frequency increases to a certain value, some energy will be absorbed and consumed by the power supply due to excessive frequency, resulting in decreased removal rate of NO and SO\textsubscript{2}.

3.3. Impacts of humidity of the exhaust gas on desulfurization and denitrification

Several experiments were performed when the voltage in two terminals of the low temperature plasma reactor is maintained at 20 kV, focusing on the impacts of humidity of the ship exhaust gas on the efficacy of desulfurization and denitrification by the low temperature plasma reactor.

Figure 2. Relationship between humidity of the ship exhaust gas and the removal rate of NO and SO\textsubscript{2}
When the voltage in two terminals of the low temperature plasma reactor is unchanged, impacts of change in humidity of the ship exhaust gas on removal rate of NO and SO$_2$ are shown in Figure 2 above. It is revealed that the removal rate of NO will decrease as the humidity of the exhaust increases; the removal rate of SO$_2$ will increase with the increase of humidity of the ship exhaust gas. H$_2$O itself can’t remove the NO, and increase of H$_2$O will consume active free radicals in the reactor, so the removal rate of NO will be decreased. H$_2$O can react with SO$_2$, and the generated sulfite ion is more easily to be oxidized, so the increase of H$_2$O will have a beneficial effect on the removal of SO$_2$.

3.4. Impacts of oxygen content of the exhaust gas on desulfurization and denitrification

Several experiments were performed when the voltage in two terminals of the low temperature plasma reactor is maintained at 20 kV, focusing on the impacts of oxygen content of the ship exhaust gas on the efficacy of desulfurization and denitrification by the low temperature plasma reactor.

When the voltage in two terminals of the low temperature plasma reactor is unchanged, impacts of change in oxygen content of the ship exhaust gas on removal rate of NO and SO$_2$ are shown in Figure 3 below. It can be seen that the removal rate of NO will decrease as the oxygen content in the exhaust gas increases. O$_2$ can absorb the electrons and form negative ions, resulting in a weaker discharge current. In addition, and O$_2$ can perform side reactions with NO. Thus, an increase in O$_2$ will reduce the removal rate of NO. The removal rate of SO$_2$ can’t be affected by the oxygen content of the ship exhaust gas.

![Figure 3. Relationship between oxygen content of the ship exhaust gas and the removal rate of NO and SO$_2$.](image)

It can be seen from the experiments that the low temperature plasma technology has a good effect on the desulfurization and denitrification of the ship exhaust gas. To treat with the ship exhaust gas with different contents of compositions, certain changes have to be made in the technical application in order to achieve the best efficacy of desulfurization and denitrification.

4. Conclusion

The sulfur oxides and nitrogen oxides contained in the ship exhaust gas will result in serious pollution to the environment. In order to take desulfurization and denitrification for the ship exhaust gas, a desulfurization and denitrification technology with low temperature plasma with dielectric barrier discharge is proposed in this study. The impacts of reactor voltage, frequency, humidity of the ship exhaust gas, and oxygen content of the exhaust gas on efficacy of the desulfurization and denitrification were studied through various experiments. The results revealed that the technology proposed in this
study can desulfurize and denitrify the ship exhaust gas better. When the voltage increases, the efficacy of desulfurization and denitrification will increase. At a voltage of 20 kV, the removal rates of NO and SO$_2$ reach 59% and 52% respectively. When the reactor voltage was maintained at 15 kV, the removal rates of NO and SO$_2$ would rise at the beginning and decrease later with increase of the frequency. The highest removal rates of NO and SO$_2$ were 55% and 42% respectively when the frequency was 10 kHz. The efficacy of desulfurization will increase as humidity increases, and the efficacy of denitrification will decrease as oxygen content increases. Researches in this study have a crucial reference value for the application of low temperature plasma technology in the desulfurization and denitrification of the ship exhaust gas. However, the scope of this study is relatively narrow, and there are still some shortcomings. In the future, some in-depth researches on practical application of the desulfurization and denitrification technology with low temperature plasma with dielectric barrier discharge in treatment of ship exhaust gas can be performed later.

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