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NOx removal by non-thermal plasma at low temperatures with amino groups additives

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Abstract–NOx removal from flue gas using direct current (DC) narrow pulsed discharge-induced non-thermal plasma (NTP) was experimentally investigated. Factors such as additives, NOx initial concentrations, residence time, reaction temperatures inside the NTP reactor, and so on were investigated to evaluate their effects on NOx removal efficiencies. The focus was on the effects of additives containing amino groups. The results showed that H_2O addition enhanced NOx removal, NH_3 could further increase the NOx removal efficiencies under the same conditions without an obvious NH_3 slip, and N_2H_4 was the most effective additive by reducing NO_x to N_2. X-Ray diffraction (XRD) analysis of the products collected from the NTP reactor demonstrated that NOx removal inside the NTP reactor was mainly based on NOx oxidation when ammonia or H_2O was used as an additive, while NOx removal was mainly based on NOx reduction with the N_2H_4 additive.

Keywords: NOx Removal, Non-thermal Plasma, Additives, Hydrazine, Ammonia

INTRODUCTION

NOx emitted from power plants and industrial combustion sources poses a serious air pollution problem. Some countries are pushing for increasingly stringent emission standards for new and existing stationary sources. In China, for new coal- and oil-fired boilers at power plants, the NOx emission limit is 100 mg/m^3, and for gas turbines the NOx limit is 50 mg/m^3 [1]. In some European countries, such as Austria and Switzerland, the NOx limit for MSW (municipal solid waste) incinerators is strictly restricted to 80 mg/m^3 [2]. To comply with such strict requirements, selective catalytic reduction (SCR) technology is required. However, by adopting SCR, the exhaust gas flow should be heated to approximately 350 °C in some cases, which consumes a great deal of energy. To find effective NOx removal technologies at temperatures below 200 °C, non-thermal plasma (NTP) technology has been receiving more attention due to its convenience and the possibility of simultaneous dust collection and NOx removal at ambient temperatures if the discharge electrode is specially designed [3].

Different types of NTPs have been developed and direct current (DC) high voltage pulsed NTP with a high-frequency represents an attractive option due to its high energy efficiency at ambient temperature and atmospheric pressure [4]. In general, in the presence of excess oxygen, NTP is essential to oxidize NO to NO_2, but cannot convert NO_2 to N_2 effectively [5]. Therefore, NTP alone cannot remove NOx effectively and NOx removal enhancement with catalysts and additives has attracted much attention [6,7]. The reported catalysts in the combined plasma-catalytic processes involve noble metals, transition metal oxides [8], metal loaded zeolites and simple metal oxides [9]. According to the position of the catalyst, the combined processes could be classified as single-stage and two-stage processes [10], where the catalyst is located inside the plasma reactor or downstream from the plasma reactor, respectively. However, the adoption of solid catalysts casts limits its application: the introduction of catalysts makes the system much more complicated, and catalysts are very expensive and sensitive to poisoning by sulfur and soot formation. Therefore, the addition of only gaseous additives to enhance NOx removal in a NTP reactor is preferred.

Mizuno et al. [11] reported that in a pulsed plasma reactor, the addition of C_2H_4 significantly enhanced the NOx removal performance at various temperatures from ambient to 220 °C. The addition of H_2O could further increase the NOx removal efficiency. In an $N_2/O_2/NO$ plasma stream, NO conversion could also be increased by 10-30% with a 5% addition of argon (Ar), which would result in increased electron densities [12]. In most cases, additives such as hydrocarbons (CH_4, C_2H_2, C_2H_4, C_3H_6) and inert gases have been used to enhance NO oxidation, and the generated NO_2 could be absorbed by aqueous solutions or decomposed using a catalyst downstream from the plasma reactor [8,9,13]. In addition to the above additives, ammonia is also used as an additive in plasma de-NOx systems to promote the NOx removal processes by oxidation and partially by reduction via NH_2 radicals [14,15] generated from NH_3 under plasmas discharge conditions [16]. Additives to enhance NOx removal based on NOx reduction are more desirable than oxidation-oriented additives, because the reduction process is much simpler. However, in a plasma reactor with NH_3 injection, the density

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of the amino groups (NH_2) is very low, whereas a hydrazine (N_2H_4) molecule contains two amino groups, which can easily decompose into NH_2 radicals and is a potential additive in the de-NOx plasma process for NOx reduction. Currently, there is little information available regarding the effect of the N_2H_4 additive in plasma reactors for NOx removal, except for its trials in the SNCR process [17,18].

Our aim was to investigate the behaviors of NOx removal from flue gases at low temperatures (ambient to 180 °C) based on a DC high voltage pulsed plasma reactor, with more attention being paid to its enhancement with simple additives, such as N_2H_4, NH_3 and H_2O, without the adoption of catalysts.

EXPERIMENTS AND METHODS

Experiments were conducted in a DCHV-3000 type coaxial cylinder NTP reactor provided by Shanghai Wanqiang Technology Development Co. Ltd., China. The NTP reactor was a needle-to-cylinder type that was energized by a 32 kV DC narrow pulsed power supply with a discharge frequency that varied from 0 to 1,000 Hz to change the energy input. The discharge zone mainly occurred in the 13 discharge tubes (diameter 85 mm and discharge gap length 1,000 mm) that were made of molybdenum glass with platinum electrodes. An activated carbon (AC) bed after the plasma reactor was adopted to adsorb the emitted reaction products. The maximum discharge power of the NTP reactor was 2,000 W, which corresponded to a discharge energy of 2 J/pulse. During the experiments, the pulse amplitude (voltage) was maintained at 32 kV, but the pulse frequency was able to be changed.

A schematic diagram of the experimental setup is shown in Fig. 1. In this system, NOx was supplied from a high-pressure NO cylinder with purity of 99.9% (Weizheng Chemical, China) and air was used as a carrier gas. The concentration of NOx was monitored online by a gas analyzer (Testo-350, Germany), and the concentration of O_3 was monitored by ozone detector tubes (Gastec, Japan). NO_2 and NH_3 were determined by a VRAE PGM-7800 (RAE, USA). To generate the hot flue gas, a liquefied petroleum gas (LPG) burner was adopted and the flue gas was a mixture of air and burnt gases produced from LPG combustion with external NO addition. The flue gas temperatures were measured at both the inlet and outlet of the NTP reactor, and the inlet temperatures of the flue gases could be changed from ambient to 180 °C. The flow rate of the simulated flue gas was controlled at 172-1,000 m^3/h, which corresponded to a residence time of 1.2 to 0.2 s in the reaction zone.

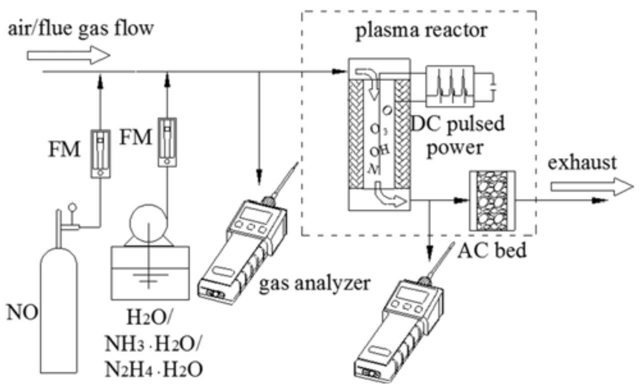

Fig. 1. Schematic diagram of the experimental setup (inlet: air or flue gas flow; FM: flow meter).

To enhance the NOx removal performance of the plasma process, compounds containing amino groups as well as H_2O were used as additives. The method atomized and sprayed a hydrazine hydrate solution, ammonia solution or deionized water into the NTP reactor from upstream. NH_3 was adopted because it has been a commonly reported additive in plasma reactors [15,19] and could be used as a baseline for evaluating the effect of the other additives. As an activating intermediate in many reactions, N_2H_4 was chosen to be an additive to improve the NOx reduction reactions in NTP reactors due to its strong reduction ability. N_2H_4 was also con- sidered to be an auxiliary additive because it improved NOx abatement in many reports [14] and it may enhance or weaken the function of NH_3 or H_2O.

During the experiments, the initial NO concentration was adjusted to 60-290 μL L^{-1} at the plasma reactor inlet by regulating the NO flow rate from the NO cylinder. Different residence times could be obtained by altering the flow rates of the simulated flue gas.

We investigated the important factors that affected the performance of NTP for NOx removal, including the initial concentrations of NOx, residence time, addition of additives and flue gas temperatures. Finally, the composition of the solid residues collected from the plasma reactor was identified by XRD (X-ray diffraction) to further understand the NOx removal mechanism.

RESULTS AND DISCUSSION

To better understand the gas-phase chemistry in the NTP, O_3 was detected when the simulated gas was only air controlled at a flow rate of 270 m^3/h. At a pulse discharge frequency of 900 Hz and ambient temperatures, a strong ozone odor was detectable and the concentration of O_3 was measured to be 40 μL L^{-1} at the outlet of the NTP reactor. Because O_3 is a highly effective oxidant, the NOx

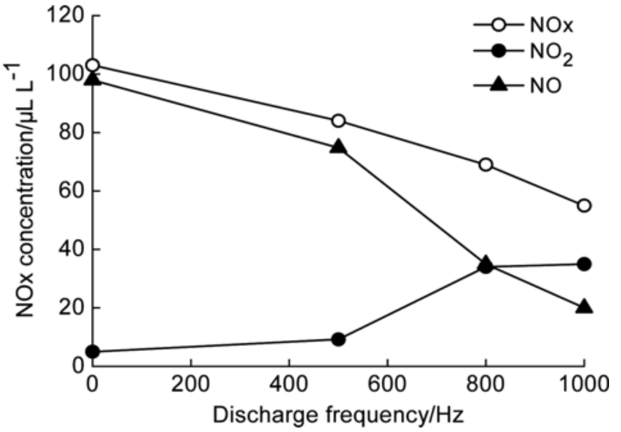

Fig. 2. NOx conversion as a function of the discharge frequency (without additives; O_2 content: 20.4%; NOx initial concentration: 103 μL L^{-1}; residence time: 0.4 s; flue gas inlet temperature: 105 °C).

removal characteristics were greatly affected. Fig. 2 shows the variations in the NOx removal efficiencies with various discharge frequencies.

As can be seen in Fig. 2, NO was partially oxidized to NO_2, and the fraction of NO_2 in NOx increased as the discharge frequency increased, which could greatly enhance the final NOx removal efficiencies if NH_3 was supplied or an alkali washing step was available. Without plasma discharge (frequency 0 Hz), NO was dominant in NOx; when the discharge frequency increased to 1,000 Hz, the fraction of NO_2 in the total NOx rose to 63.6%. This was because NTP was effective at oxidizing NO to NO_2 by producing O_3 in an oxygen-containing atmosphere. Wang et al. [20] confirmed that NO could be oxidized into NO_2, NO_3 and N_2O_5 by O_3 through the following reactions: $NO+O_3=NO_2+O_2$, $NO+O+M=NO_2+M$, $NO_2+O_3=NO_3+O_2$, $NO_2+O=NO_3$, $NO_2+NO_3=N_2O_5$. NO_2 was the main product when the molar ratio of O_3/NO was below 1.0. As shown in Fig. 2, at a discharge frequency of 1,000 Hz, the NOx removal ratio was 46.6%, while the NO removal ratio was 79.6%.

In practice, a flue gas stream always contains a certain level of water vapor that can generate OH radicals by an electric discharge dissolving NO_2 to form nitric acid. Nitric acid can easily be washed away from the flue gas during the washing steps. Therefore, in the gas-phase reactions initiated by NTP, the oxidation of NO to NO_2 with the assistance of O_3 and OH radicals is an important step in NOx abatement, as reported by other researchers [9].

1. Effect of the Initial NOx Concentration

The experiment was performed at ambient temperature, and the temperature in the discharge zone was approximately 44 °C. The carrier gas was saturated moist air. Throughout testing, the O_2 concentrations were maintained at a high level (19.5-20.6%) and the initial NOx concentrations were adjusted to 63 $\mu L\ L^{-1}$, 131 $\mu L\ L^{-1}$ and 198 $\mu L\ L^{-1}$. At these different initial NOx levels, the flow rate of the simulated gas was kept at 1,000 m^3/h (corresponding to a residence time of 0.2 s). The relationships among the NOx removal ratios, discharge frequencies and NOx initial levels are presented in Fig. 3.

Fig. 3 indicates that the NOx removal efficiencies decreased as the initial concentrations of NOx increased. At a frequency of 1,000 Hz, as the initial concentrations of NOx increased from 63 $\mu L\ L^{-1}$ to 198 $\mu L\ L^{-1}$, the removal efficiencies declined from 68.3% to 29.3%. This result was because high initial NOx concentrations required more reactive species (such as radicals and electrons) to attain the same removal ratios, leading to an increase in power consumption. At the same discharge frequency (the same energy input), an increase in the initial NOx concentrations was related to a decrease in the specific energy density, as confirmed in previous studies [21]. However, at a frequency of 100 Hz, the low initial levels of NOx did not perform better in NOx abatement because a residence time of 0.2 s was not sufficient to reach the steady state for the plasma chemical reactions in the electrical field. The effect of residence time on NOx removal efficiencies will be discussed later.

In addition, the discharge frequency was another important factor in NOx removal. The data from Fig. 3 show that the NOx removal efficiencies increased with the increasing pulse frequency, and there was a good linear relationship between the pulse frequency and NOx removal efficiency. This result was because a higher pulse frequency corresponded to a higher energy input and correlated to more reactive electrons, which could further promote radical species generation. The results proved that a high-frequency discharge enhanced the NOx removal reactions.

2. Effect of Residence Time (τ)

To design an NTP reactor or to define the gas flow rate (treatment capacity), it is important to allow for a sufficient reaction time. The relationship between the reaction time and NOx removal efficiency could provide this information. To determine the effect of residence time on NOx removal, experiments were performed at various residence times (0.44 s, 0.51 s, 0.61 s) by changing the flow rates of the simulated flue gas through the NTP reactor and holding the inlet gas temperature, O_2 level and NOx initial concentration constant at 105 °C, 20.4% and 118 $\mu L\ L^{-1}$, respectively. The experimental results, presented in Fig. 4, show that a longer resi-

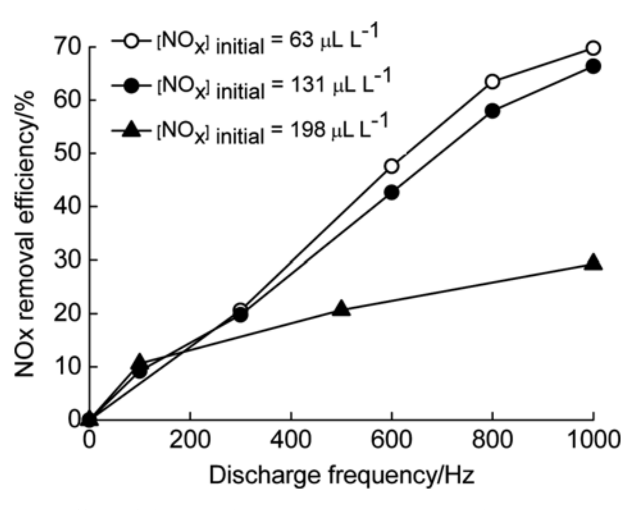

Fig. 3. Effect of the initial NOx concentrations on the NOx removal efficiencies (without additives; O_2 content: 19.5-20.6%; residence time: 0.2 s; flue gas inlet temperature: 44 °C).

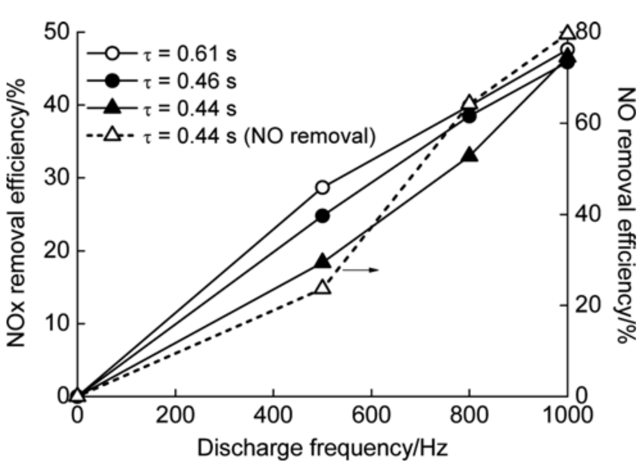

Fig. 4. Effect of residence time on the NOx removal efficiencies (without additives; O_2 content: 20.4%; NOx initial concentration: 118 $\mu L\ L^{-1}$; flue gas inlet temperature: 105 °C; water vapor partial pressure: 0.81%).

dence time generally resulted in an increase in the NOx removal efficiency. At a frequency of 500 Hz, as the residence time increased from 0.44 s to 0.61 s, the NOx removal efficiency increased from 18.4% to 28.7%. At a frequency of 800 Hz, the NOx removal efficiency increased with longer residence times, but the growth rates decreased. At the peak discharge frequency (1,000 Hz), the NOx removal ratio appeared to be independent of residence time, which may because at a frequency of 1,000 Hz, the residence time of 0.44 s was sufficient for the reactions that took place, but at a lower discharge frequency, a longer reaction time was favored because the interaction time for the radicals with NOx molecules and the duration of the energetic species acceleration in the electric field increased at low frequencies [22]. The results obtained here suggested that in an NTP reactor, sufficient time was allowed for plasma chemical reactions to occur, and lower discharge frequencies required longer residence time to reach equilibrium. As the pulse discharge frequency increased, the treatment capacity rose for the same NTP reactor.

The NO removal efficiency versus discharge frequency at a residence time of 0.44 s is shown in Fig. 4. It can be seen that under the same conditions, the removal ratio of NO was much greater than that of NOx, especially at high discharge frequencies. For example, the NOx removal efficiency was only 33.0% at a frequency of 800 Hz and 46.6% at a frequency of 1,000 Hz, while the NO removal ratio could be up to 64.3% and 79.6%. This could be explained by a high discharge frequency being favorable to NO into NO_2 conversion. NO_2 is water soluble and can be removed by alkaline wet scrubbers through the following reactions:

$$2NO_2+2NaOH=NaNO_2+NaNO_3+H_2O \qquad (1)$$

$$NO+NO_2+2NaOH=2NaNO_2+H_2O \qquad (2)$$

Therefore, the NOx removal ratio could be enhanced significantly if an alkaline scrubber is equipped after the NTP reactor.

3. Effect of Additives

Based on the fact that NO_2 and NO_3 or N_2O_5 form inside the NTP reactor, the presence of NH_3 in the flue gas could further neutralize these acidic gases into NH_4NO_3. In this research, the effects caused by adding hydrazine hydrate ($N_2H_4 \cdot H_2O$), ammonia (NH_3) and moisture were checked. Under the conditions of 105 °C, 20.4% O_2 and 0.81% partial pressure of water vapor in the flue gas, the initial NOx level was controlled between 103 and 121 μL L^{-1} and the gas flow rate was adjusted to maintain a residence time of 0.5 s inside the NTP reactor. Then, a 2.28% hydrazine hydrate solution, 1.73% ammonia solution or deionized water was spiked into the plasma reactor, and their mass flow rates were controlled at approximately 49 mL min^{-1}. At this flow rate, the NH_2/NO molar ratio for both the ammonia solution and hydrazine hydrate solution was kept at 1.2, and the absolute moisture content of the flue gas with these three types of injection additives was increased by 1.03%. The impacts of N_2H_4, NH_3 and H_2O on NOx removal are described in Fig. 5.

From Fig. 5, it can be seen that moisture positively affected NOx removal. Exemplified at a frequency of 500 Hz, the degree of NOx removal increased from 18.4% to 31.4% with moisture (H_2O) addition, but this increase was smaller at higher discharge frequencies because more NO_2 was formed, which also contributed to NOx emissions. An additional NH_3 spike could further increase the NOx removal efficiency, especially at high discharge frequencies, which may be caused by more NO_2 forming at high discharge frequencies and ammonia could react with acidic NO_2 through the following reactions:

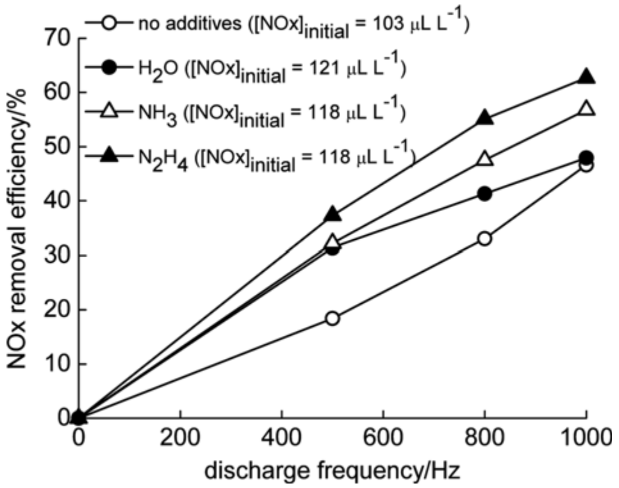

Fig. 5. Effect of N_2H_4, NH_3 and H_2O addition on the NOx removal efficiencies (O_2 content: 20.4%; NOx initial concentration: 103-121 μL L^{-1}; residence time: 0.5 s; flue gas inlet temperature: 105 °C; water vapor partial pressure: 0.81%).

$$2NH_3+2NO_2+H_2O=NH_4NO_3+NH_4NO_2 \qquad (3)$$

$$NO+NO_2+2NH_3+H_2O=2NH_4NO_2 \qquad (4)$$

$$NH_4NO_2=N_2+2H_2O \qquad (5)$$

The results in Fig. 5 indicated that the N_2H_4 spike was more effective in the discharge zone for NOx removal. This was because the activation of N_2H_4 and rupture of the N-N bond into NH_2 [18] may be stimulated by a pulse discharge through the following reactions: $N_2H_4+e^* \rightarrow N_2H_4^*+e$, $N_2H_4^* \rightarrow 2NH_2$ [23], where the asterisk represented an excited or activated state. It was demonstrated that the N-N bond in N_2H_4 was weaker than that in NH_3, and the main path of N_2H_4 decomposition was the direct rupture of the N-N bond to create NH_2 regardless of the concentrations of O, H and OH radicals [24]. Consequently, N_2H_4 formed more NH_2 than NH_3. Furthermore, NH_2 could be transformed into H by O radicals through the following reaction: $NH_2+O \rightarrow HNO+H$. Then, the H radicals were involved in NO oxidation through the following channel: $H \rightarrow HO_2 \rightarrow NO_2$ [19]. NH_2 could also promote NO reduction to N_2. Therefore, N_2H_4 combined with the addition of moisture exhibited a synergistic effect on NOx abatement.

In plasma reactions, OH radicals were regarded as one of the most important species because of their strong oxidation, which could be produced through the dissociative ionization of H_2O at its excited state. To investigate the effect of water vapor content on the NOx removal behavior, experiments were performed at three different moisture spraying rates of 1.03%, 2.4% and 3.4%, which corresponded to absolute moisture content of 2.06%, 3.43% and 4.43%, respectively. Note that when the spraying rate of 3.4% was

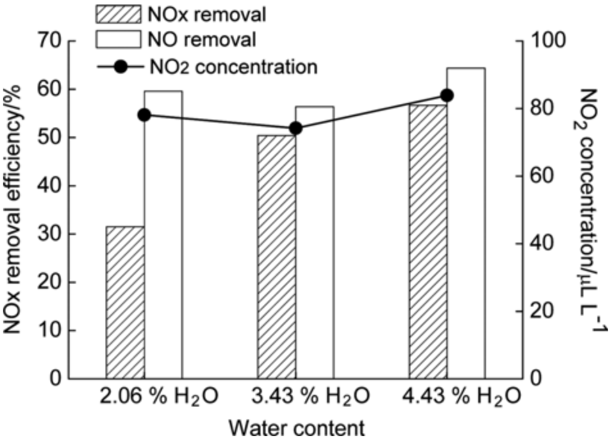

Fig. 6. Effect of water content on the NOx removal efficiencies (O_2 content: 19.85%; NOx initial concentration: 127 μL L^{-1}; residence time: 0.54 s; pulse frequency: 1,000 Hz; flue gas inlet temperature: 150 °C; water vapor partial pressure: 1.03%).

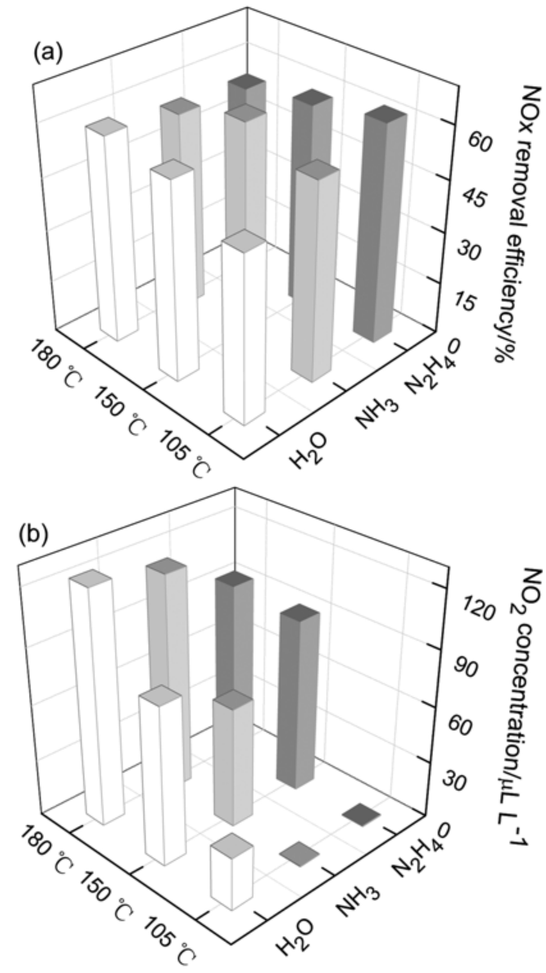

Fig. 7. Effect of temperature on the NOx removal efficiencies (absolute water vapor content: 2.06% at 105 °C, 4.43% at 150 °C, 3.43% at 180 °C; O_2 content: 19-20.4%; NOx initial concentration: 118 μL L^{-1} at 105 °C & 150 °C, 238 μL L^{-1} at 180 °C; residence time: 0.5 s at 105 °C & 150 °C, 1 s at 180 °C; pulse frequency: 1,000 Hz).

tested, the flue gas was over-saturated and water drops could be seen from the outlet of the NTP reactor. From Fig. 6, it can be seen that as the moisture content increased, the degree of NOx removal increased at the 1,000 Hz frequency. When the moisture content varied from 2.06% to 4.43%, the NOx removal ratio increased from 31.5% to 56.7%, while the removal ratio of NO increased from 56.4% to 64.4%. Fig. 6 also shows that the degree of NO removal was associated with the formation of NO_2, and a large amount of NO_2 was generated (up to 74.2-83.9 μL L^{-1} with 1.03-3.4% moisture injection). An assumption was made that the oxidation of NO to NO_2 was promoted by the involvement of OH radicals produced by H_2O. However, as the moisture content increased, NO_2 could also react with water vapor through the flowing reaction: $3NO_2+H_2O=2HNO_3+NO$. Therefore, moisture spraying did not always promote NO removal and there was an appropriate moisture level.

4. Effect of Temperature

The effect of the flue gas inlet temperature on NOx removal was also examined in this research, as presented in Fig. 7. Fig. 7 indicates that temperature was not a decisive factor, but did influence the function of the additives and the formation of NO_2. In general the NTP reactor successfully removed NOx when the temperature changed from 105 °C to 180 °C. From Fig. 3, the NTP reactor was also efficient in NOx abatement at ambient temperatures. Thus, the NTP reactor was effective for NOx removal over a temperature range of ambient to 180 °C. Mok et al. [25] also confirmed that a reaction temperature that ranged from 75 to 200 °C did not greatly affect the NOx removal efficiencies. Bröer et al. [26] found that the NOx removal ratio only varied from 10% to 18% within a gas temperature range of 100 to 250 °C. Li et al. [13] reported that the degree of NOx removal was almost stable within a temperature range of 200 to 550 °C in plasma reactions.

However, when additives were introduced, the NOx removal behavior changed as the temperature varied. The data in Fig. 7 show that N_2H_4 was most effective for NOx removal at 105 °C, but N_2H_4 did not exhibit better performance than NH_3 or moisture at a temperature above 150 °C. This was probably because N_2H_4 easily decomposed at temperatures higher than 150 °C and its thermal decomposition became vigorous at temperatures higher than 260 °C [27]. During the experiments, to completely vaporize water, all of the additives (hydrazine hydrate solution, ammonia solution and deionized water) were injected into the flue gas in high temperature zones upstream of the NTP reactor. At high temperatures, N_2H_4 was unstable and decomposed into N_2, H_2 and NH_3, which actually cancelled its ability to remove NOx. There was a difference for the NH_3 additive spray as the temperature increased because reactions (3) and (4) were hindered at higher temperatures, as demonstrated by the high NO_2 concentrations, as shown in Fig. 7(b). Therefore, the introduction of an additive (N_2H_4 or NH_3) was favorable only when the temperature was below 150 °C.

As mentioned above, the fractions of NO_2 in NOx were significantly affected by temperature, and the NO_2 concentration considerably increased as the temperature increased, as depicted in Fig. 7(b). The results were in agreement with Mok et al.'s findings [25]. However, Leray et al. [28] studied NOx removal from simulated diesel engine exhaust (containing the H_2O and hydrocarbon additives) using a dielectric barrier discharge (DBD) reactor and found that the NO_2 concentration increased as the temperature increased from 80 °C to 118 °C, and then, the concentration decreased slightly when the temperature ranged from 118 to 200 °C. Tang et al. [29] stated that the conversion of NO in the DBD plasma slightly declined when the temperature varied from 50 °C to 250 °C. Although the impact mechanism of temperature was unclear, it was believed that an increase in temperature could increase the electron collision frequency and excited particle reaction rate, but it also promoted the disappearance of some radicals at the same time. In addition, the reaction rates of NO_2 with NH_3 to form NH_4NO_3 (as below) increased as the reaction temperature decreased [25].

$$2NO_2+2NH_3=N_2+H_2O+NH_4NO_3\ (s) \tag{6}$$

At temperatures below 75 °C, NO_2 sequestration as solid NH_4NO_3 became important. Therefore, the fraction of NO_2 in NOx decreased at low temperatures in the presence of N_2H_4 or NH_3.

Although additives such as N_2H_4, NH_3 and H_2O could enhance NO oxidation, the oxidized product of NO_2 could be easily removed by photocatalytic processes involving TiO_2 [30], SCR [31], AC adsorption [32] or absorption with alkaline solutions (such as NaOH, Na_2SO_3, $(NH_4)_2CO_3$ [33]). In this research, more than 60% of the NOx removal efficiencies could be obtained by choosing proper additives at suitable temperatures in a simple, low energy input NTP reactor. Because NO_2 is easily removed from NOx gases, NTP is a promising candidate for controlling NOx emissions.

In addition, when an ammonia solution was used as an additive, even the NH_3 concentration was above 200 μL L^{-1} at the inlet of the NTP reactor, which was above the range of the VRAE PGM-7800. The NH_3 slip concentration at the outlet was only 3-4 μL L^{-1} at ambient temperatures and was not detectable at higher temperatures, which was quite different from the other de-NOx processes, such as the SCR process. As for N_2H_4 spraying, no NH_3 slip was detected. Therefore, the NTP reactor tested here effectively prevented NH_3 slip in the de-NOx processes.

ANALYSIS OF THE REACTION PRODUCTS

After several groups of experiments, the discharge electrode was observed to be covered with white salt crystals, as can be seen in Fig. 8(a), which may have led to an insufficient plasma discharge energy. In addition to the surface coverage of the discharge electrode, the AC adsorption bed was also covered with white salts (see Fig. 8(b)).

Fig. 8. Salt formation during the plasma reactions.
(a) Covered on the discharge electrode
(b) Attached on the surface of activated carbon

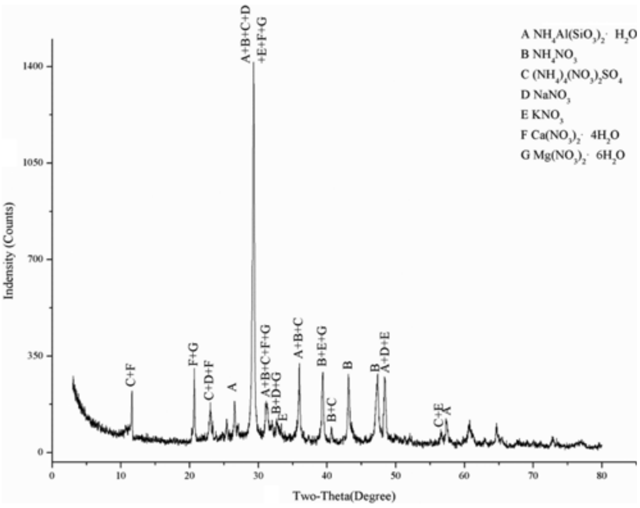

Fig. 9. XRD pattern of the residue from the plasma reactor.

The XRD results of the salts collected from the plasma reactor are presented in Fig. 9. It was found that NOx was mainly converted to nitrates, such as NH_4NO_3, $NaNO_3$, KNO_3 and other nitrate salts, by pulsed discharge plasma with the addition of ammonia. The introduction of elements such as Na, K, Al, Ca and Mg may have been caused by the residual ash in the flue. No nitrites were detected in the XRD pattern of the salts because nitrites were easily oxidized to nitrates through the following reaction: $2NaNO_2+O_2=2NaNO_3$. The XRD analysis revealed that there were no harmful by-products. It could be concluded that in an oxygen-rich NTP reactor, NOx removal was mainly based on the oxidation processes and NH_3 could be spiked to neutralize the products and enhance the removal of NOx with the help of a moisture adjustment. However, some measures should be taken to prevent the products from precipitating on the electrode.

CONCLUSIONS

This study showed that NOx could be effectively removed in a pulsed discharge non-thermal plasma reactor with the gas inlet temperature ranging from ambient to 180 °C, and the NOx removal performance was greatly influenced by the initial NOx concentrations, discharge frequency, residence time and addition of additives. The following conclusions could be drawn from the experimental results:

(1) Under the conditions of a discharge frequency of 1,000 Hz and residence time of 0.2 s, the NOx removal efficiency decreased from 68.3% to 29.3% as the initial concentration of NOx increased from 63 μL L^{-1} to 198 μL L^{-1}. For the impact of discharge frequencies, the data showed that at an NOx initial concentration of 36 μL L^{-1} and a residence time of 0.2 s, the NOx removal ratio increased from 0 to 68.3% with the discharge frequency increasing from 0 Hz to 1,000 Hz. Our study indicated that high initial NOx concentrations negatively affected NOx removal, while the NOx re-

moval ratio increased with discharge frequency, and good linear relationships were observed between the NOx removal efficiency and the discharge frequency. For both factors, the energy density was a decisive cause.

(2) The testing results showed that at a frequency of 500 Hz and a NOx initial concentration of 118 μL L^{-1}, the NOx removal efficiency increased from 18.4% to 28.7% as the residence time increased from 0.44 s to 0.61 s, while at the peak discharge frequency of 1,000 Hz, the NOx removal ratio was nearly independent of the residence time. It could be concluded that an increase in the residence time could lead to an increase in the NOx removal efficiencies, and the required reaction time was different at different discharge frequencies. Less time was needed at high discharge frequencies. To attain certain NOx removal efficiencies, a sufficient residence time should be ensured.

(3) Three tested additives, N_2H_4, NH_3 and H_2O, all enhanced the removal of NOx under different discharge frequencies, of which N_2H_4 was the most effective by reducing NO_x to N_2. NH_3 was the second most effective additive by neutralizing the oxidation products of NOx. The addition of moisture helped generate OH radicals to enhance NOx oxidation. The NH_3 slip was inhibited in the NTP reactor when N_2H_4 or NH_3 was used as an additive.

(4) The NTP reactor was effective for NOx abatement when the inlet gas temperature ranged from ambient to 180 °C, and the temperature did not have decisive effects on NOx abatement. However, the temperature significantly influenced the fractions of NO_2 in NOx and affected the function of the additives. Higher temperatures produced more NO_2, which could be washed away in an alkali scrubber. N_2H_4 and NH_3 were not effective as the temperature increased, whereas the addition of H_2O was favored at higher temperatures.

(5) The XRD results showed that salts collected from the plasma reactor were mainly nitrates, such as NH_4NO_3 and $NaNO_3$, which proved that NOx abatement in a NTP reactor was mainly caused by oxidation.

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