NO to NO₂ and Nitric Acid Conversion by Corona Induced Non-Thermal Plasmas and H₂O₂ Scrubbing

Student Member Keping Yan, Member Seiji Kanazawa, Member Toshikazu Ohkubo

Member Yukiharu Nomoto (Oita University, Japan)

Keywords: Streamer Corona, Chemical Kinetics, Non-thermal Plasma, NO_x Removal, H₂O₂ Scrubbing

1. Introduction

In order to increase the energy efficiency for NO_x and SO₂ removal, pulsed streamer corona induced non-thermal plasmas have been used as wet and/or semi-wet processes for enhancing heterogeneous reactions and chemical absorption^(1,2). DC Corona enhanced SO₂ and nitric gases absorption has been known for many years^(3,4). However, the effects of DC corona modes of glow and streamer on the absorption or chemical reactions have not been identified in previous work, for which the glow discharge induces negligible chemical reactions⁽⁵⁾. On the other hand, H₂O₂ enhanced NO_x absorption has also been well known⁽⁶⁾. Civitano also used H₂O₂ injection for enhancing NO_x and SO₂ removal and reducing NH₃ slip during the plasma treatment⁽¹⁾. Our previous studies show that for oxygen-rich exhaust gases treatment by corona induced plasma, the reverse reaction to convert NO₂ to NO via O radicals would play the key role for determining NO_x removal efficiency⁽⁷⁾. This work reports the NO to NO₂ and nitric acid conversion with corona induced non-thermal plasmas and H₂O₂ scrubbing. The main objective is to control the produced NO₂ concentration and limit the reverse reaction during NO removal.

2. Experimental Set-Up

Fig.1 shows the schematic of the experimental set-up with one nozzle electrode reactor. The electrode geometry, power supply and measurement systems are the same as the previous one^(5,8). A mixture liquid (22cm³) of distilled water (70%) and H₂O₂ (30%) in a stainless steel container is used as the ground electrode. The gap distance

Fig. 1: Schematic of the experimental set-up.

between the nozzle electrode and liquid surface is about 40 mm. Experiments are carried out at room temperature and under atmospheric pressure in gas mixtures of N₂+O₂(15-20%)+CO₂(0-10%)+NO_x. The total gas flow rate is between 4.0 L/min and 7.0 L/min.

3. Results and Discussions

With increasing the applied voltage, streamers propagate from the nozzle to the liquid. When the voltage is increased to about 23 kV, streamer could bridge the gap and arrive at the liquid surface. As a result, both gas phase and aqueous phase reactions could be induced. In the case of glow discharge, NO oxidation and NO_x absorption by the plasma and liquid are negligible because the plasma is restricted at the tip of nozzle electrode. Under streamer corona, both the removed NO and the produced NO₂ increase with increasing the applied voltage. As an example, Fig.2 shows typical results of the NO to NO₂ conversion under various initial NO concentrations with the dry⁽⁷⁾ and present systems. For the oxygen rich mixtures of N₂+O₂(≥3.6%)+CO₂+NO_x, almost 100% of the removed NO would be oxidized to NO₂ with the dry type reactor. The less amount of produced NO₂ per unit removed NO with the present system is due to the aqueous related chemical reactions and absorption. Near the streamer onset, about 100% of NO is converted to NO₂, where main reactions occur in gas phase due to the smaller plasma region; while after streamer contacting the liquid surface, the conversion ratio decreases to about 55%, where both gas and aqueous phase reactions would

Fig.2: Typical NO to NO₂ conversion under various initial NO concentrations with dry and present systems.

play important role. If only using H₂O liquid film, the conversion ratio is about 65%. As observed in wet ESP model ⁽⁹⁾ and in traditional H₂O₂ scrubber ⁽⁶⁾, HNO₃ acid would be the final end by-product for the present system.

In order to explain the effects of the aqueous phase, considering a system with a gas flow rate of F_g and H₂O liquid flow rate of F_L , and according to the Henry's law ⁽¹⁰⁾, the equilibrium of species A between the gas phase and the liquid phase can be expressed by the equation (1) and its percentage in the H₂O liquid phase can be derived as the equation (2).

$$A(g) \rightleftharpoons A(aq) \quad (1)$$

$$\eta_l = \frac{H_a \cdot R \cdot T \cdot F_L / F_g}{1 + H_a \cdot R \cdot T \cdot F_L / F_g} \quad (2)$$

where $A(g)$ and $A(aq)$ are gas phase and aqueous phase concentrations. η_l , H_a , T and R are the percentage in the aqueous phase, Henry's law coefficient ⁽¹⁰⁾, temperature and the ideal gas constant, respectively. Fig.3 shows the relationship between the Henry's law constant and the percentage in the liquid phase in terms of the equation (2). The percentage η_l only reflects the physical solubility of gases.

Radicals produced by plasma could convert relatively insoluble species, such as NO and NO₂, to very soluble compounds, such as HNO₂, HNO₃, NO₃ and N₂O₅ as shown in Fig. 3. Moreover, for the present system, H₂O₂ in the liquid phase could also lead to oxide HNO₂ to HNO₃. The main chemical reaction pathways are shown in Fig.4. Very complicated aqueous phase plasma induced chemical

Fig.3: Dependence of the ratio in H₂O liquid phase on the Henry's law constant at 298K.

reactions may also occur at the prior equilibrium between the gas and liquid phases. As a result, much more pollutants may be absorbed in the aqueous phase due to plasma induced reactions. The energy efficiency for NO_x removal is also increased with the present system in contrast to the dry type and the H₂O liquid film wet type reactor. The efficiency of the tradition NO_x scrubber may be also improved if integrating them with plasma because of radicals production. However, a detailed physical and chemical model study is far from complete for such kinds of plasma system.

(Manuscript received Dec. 4, 1998, revised April 19, 1999)

Fig.4: Main chemical reaction pathways for NO_x conversion with corona induced non-thermal plasma and H₂O₂ scrubbing.

References

- (1) Civitano L.: *HAKONE IV*, Bratislava, p.Vii-Xiii (1993)
- (2) Mizuno A. et al.: *IEEE Trans IAS*, **31**, 1463-1467 (1995)
- (3) Adachi T.: *Trans IEE Japan B*, 512-517 (1977)
- (4) Vasishtha N. et al.: *Ind. Eng. Chem. Res.*, **27**, 1235-1241 (1988)
- (5) Yan K., et al.: *Journal of Electrostatics*, (1998) (in press)
- (6) Thomas D. et al.: *Ind. Eng. Chem. Res.*, **36**, 3315-3322 (1997)
- (7) Yan K., et al.: *Plasma Chem. and Plasma Proc.*, (1998) (in press)
- (8) Yan K., et al.: *Trans IEE Japan*, **118-A**, 948-953 (1998)
- (9) Dors M., et al.: *J. of Electrostatics*, **45**, 25-36 (1998)
- (10) Seinfeld J.H. and Pandis S.N.: *Atmospheric chemistry and physics*, John Wiley & Sons, Inc., p. 340-341 (1997)

Keping Yan (Student-member) was born in Shanxi, China, in 1962. He obtained B.S. and M.S. degrees in Applied Physics from Beijing Institute of Technology, China, in 1983 and 1986, respectively. Since 1988, he has been involved in corona induced non-thermal plasmas for pollutants control. He is one of co-authors for about 40 publications. He joined Oita University as a PhD course student in the April, 1997.

Seiji Kanazawa (Member) see *Trans IEE Japan*, Vol.119-A, No.6 (1999)

Toshikazu Ohkubo (Member) see *Trans IEE Japan*, Vol.119-A, No.6 (1999)

Yukiharu Nomoto (Member) see *Trans IEE Japan*, Vol.119-A, No.6 (1999)