Simultaneous NO_x/SO_2 removal by ammonia gas excited by atmospheric plasma

Shinji Kambara*, Yukio Hayakawa, Kazuhiro Kumabe, Hiroshi Moritomi
Gifu University
Graduate school of Engineering, Environmental and Renewable Energy Systems Division
1-1 Yanagido, 501-1193, Japan

and **Megumi Masui**
ACTREE CORPORATION
375 Misumimachi, Hakusan, Ishikawa, 924-0053, Japan

*E-mail: kambara@gifu-u.ac.jp

ABSTRACT

The ammonia radical injection method have been developed to expand window temperature and to improve NO removal efficiency in the conventional SNCR. Ammonia radicals (NHi) were generated by atomospheric pressure plasma. In this paper, characteristics of simultaneous NO/SO_2 removal were investigated. Both NO and SO_2 removal by the radical injection in $NO/SO_2/O_2/N_2$ system method were higher than that in $NO//O_2/N_2$ or $SO_2/O_2/N_2$ system. Above 90% NO removal was atained at 700ºC at molar ratio of 1.5.

1. INTRODUCTION

Removal of nitrogen oxides (NO_x) from flue gases emitted from stationary combustors is desirable for environmental pollution control and public health. In Japan, strict emission limits are in place for all stationary sources, including small-scale combustion plants such as waste incinerators. Although combustion modifications involving low-NO_x burners and the two-stage combustion methods contribute to reducing NO_x emissions, NO_x treatment techniques are also usually required to meet the strict NO_x emission limits. Selective catalytic reduction (SCR), an efficient treatment technology, has been used world-wide for NO_x removal in large-scale combustors such as coal-fired power plants. However, a drawback of SCR systems in application to coal combustion of high sulfur coals is that they are particularly costly because frequent replacement of the catalyst is required owing to catalyst poisoning by sulfur dioxide.

For use of high sulfur coals, another possibility for NO_x removal is to adopt selective non catalytic reduction (SNCR) techniques. SNCR systems utilize a conceptually simple process that involves injecting molecular ammonia into the furnace without using a catalyst. However, drawbacks of SNCR are the narrow temperature window and insufficient efficiecy of NO_x removal.

To solve the problems in the SNCR, a unique NO_x removal by ammonia radical injection using an intermittent dielectric barrier discharge (DBD) have been developed for flue gas clean-up [1-5]. In this paper, characteristics of simultaneous NOx/SO_2 removal were investigated.

2. EXPERIMENT

Figure 1 depicts a schematic diagram of the ammonia radical injection system using the pulsed DBD (non-thermal plasma). The facilities contains two gold furnaces with quartz tubes for controlling gas temperature, model gas ($NO/SO_2/N_2/O_2$) supply system, NH_3/Ar supply system, radical injector, mixing chamber, high voltage pulsed power supply, and gas analyzers (NO_x/O_2, SO_2, N_2O). The quartz tubes installed in the pre- and post- heater have a 46 mm inner diameter, and are 500 and 600 mm in length, respectively.

The initial concentrations of NO and SO_2 in the total flow were fixed at 500 and 250 ppmv, respectively, and O_2 concentrations adjusted 2.1 or 8.3 vol%. Temperature of pre-heater fixed at 500ºC, while temperature of reaction heater varied from 500−800ºC.

An NH_3/Ar gas mixture was supplied to radical injector as simultaneous NO_x/SO_2 removal agent. The NH_3 concentration in the radical injector was 2460ppm or 3936ppm, and the flow rate was 0.31 SLM or 0.46 SLM. An $NH_3/(NO+SO_2)$ molar ratio set 1.0 or 1.5. Total flow rate of model gas and the removal agent fixed at 3.0 SLM.

In the radical injector, atmospheric pressure plasma is occured by using pulse power supply (SAWAFUJI

ELECTRIC CO., LTD). The radical injector is inserted into the mixing chamber, which is 61 mm in diameter and 490 mm long. The electrodes of the radical injector are coaxial in configuration, with quartz glass tubes as the dielectric materials. The high voltage electrode (SUS316), which is 50 mm in a diameter and 500 mm long, is installed into the inner quartz tube. The outer tube is 61 mm in a diameter, 2 mm in thickness, and 490 mm in length. The ground electrode (SUS316, punching metal), which is 360 mm long and 0.2 mm, covers the outer side of the outer glass tube.

The applied voltage by pulse power supply varied from 3 to 15 kV. The frequency of pulse power supply fixed 10 kHz.
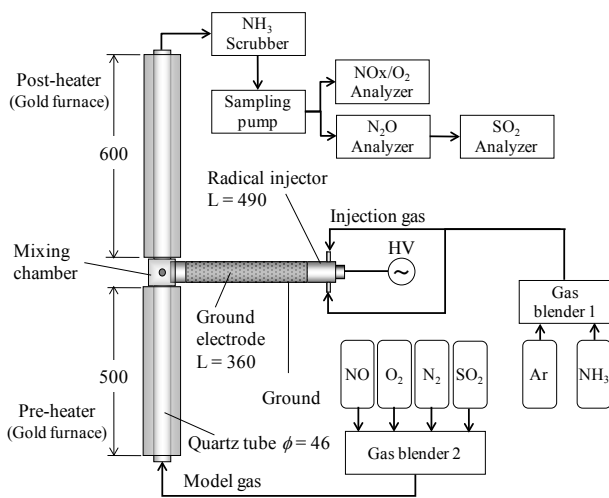

Fig.1 Schematic diagrams of experimental apparatus.

3. RESULTS AND DISCUSSION

3.1 Characteristics of NO removal by radical injection

Figure 2 shows variation in NO removal at various applied voltage and reaction temperatures ranged from 500 to 750ºC. NO removal was observed to suddenly increase at a boundary of the applied voltage, and gradually decrease for progressively greater applied voltages after a maximum level. The boundary of the applied voltage was observed to vary with reaction temperatures. A higher percentage of NO removal was observed at the lowest applied voltage and the highest reaction temperature.

It seemed that most effective radical for DeNOx (NH$_2$ radical) was formed at the low applied voltage, therefore high NO removal was attained at lower sides of the applied voltage.

The maxmum values of NO removal by the radical injection method at each temperature in Fig.2 were compared with NO removal by thermal DeNOx in **Figure 3**. In the radical injection method,

an increase of NOx removal observed above 600ºC: it clearly indicates that the radical injection broadened the temperature window and lowered its starting temperature (in comparison to thermal DeNOx). The temperature shift was 150 °C at an NO removal of 20%.
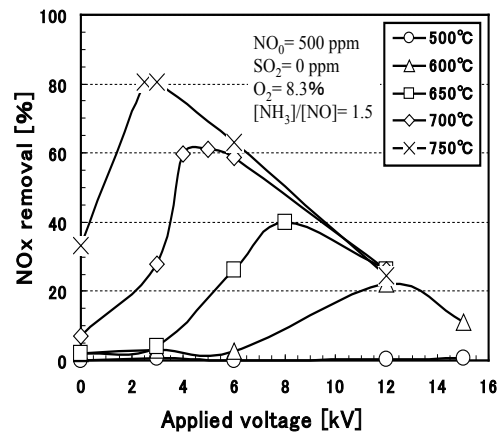
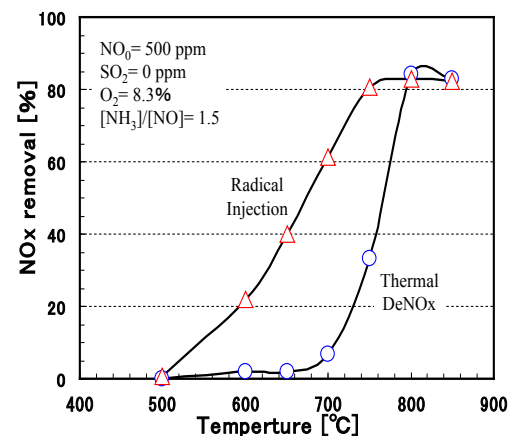

Fig.2 Characteristics of NO removal by radical injection.

Fig.3 Comparison of NO$_x$ removal characteristics between radical injection and thermal De-NO$_x$.

3.2 Simultaneous NO/SO$_2$ removal by radical injection

Figure 4 shows change of NO removal in various reaction temperatures in independent and simultaneous removal by the radical injection method. Experimental conditions indicate in Fig. 4, where M_R is molar ratio calculated by [NH$_3$]/[NO+SO$_2$]. It found that NO removal was promoted under the simultaneous removal condition: above 90% NO removal was attained at 700ºC.

On the other hand, maxuimum levels of SO$_2$ removal was observed at 600ºC, and SO$_2$ removal was decreased with an increase of reaction temperatures as shown in **Figure 5**. SO$_2$ removal in simultaneous removal tests was increased in compared to independent tests.
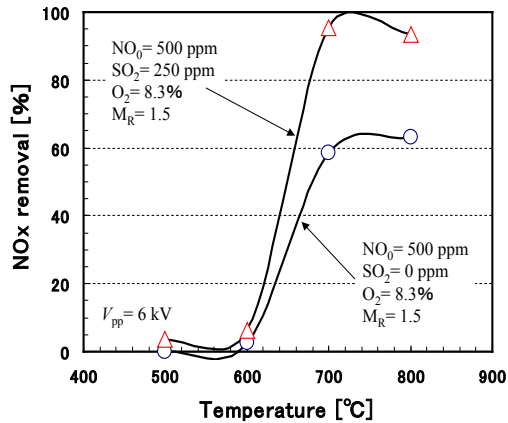
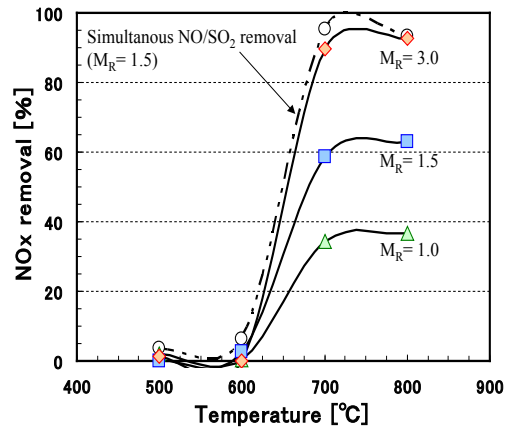Fig.4 Characteristics of NO removal in simultaneous NOx/SO$_2$ removal reaction.
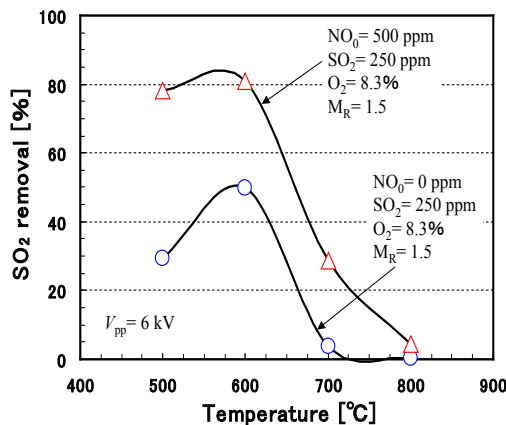

Fig.6 Effect of molar ratios on NOx removal.

Fig.5 Characteristics of SO$_2$ removal in simultaneous NOx/SO$_2$ removal reaction.

4. CONCLUSION

Simultanous NO/SO$_2$ removal tests by radical injection method were carried out. The removal agent, molecualr ammonia, was excited by the atomspheric pressure plasma, and was injected into the model gases (NO/SO$_2$/O$_2$/N$_2$ system, NO//O$_2$/N$_2$ system, SO$_2$/O$_2$/N$_2$ system).

In simultaneous removal tests, NO removal was promoted under the simultaneous removal condition: above 90% NO removal was attained at 700ºC. Besides SO$_2$ removal was increased in NO/SO$_2$/O$_2$/N$_2$ system. Effectiveness of NO and SO$_2$ removal acceralation was explaned by the deference of reaction rate between NO-NH$_3$ system and SO$_2$-NH$_3$ system.

Effectiveness of NO and SO$_2$ removal acceralation in simultaneous removal tests shown in Figs. 5 and 6 can be explained the following:

Most important factor is the deference of reactivity between NO-NH$_3$ system and SO$_2$-NH$_3$ system. The reaction rate of NO removal is faster than that of SO$_2$ removal, therefore injected NH$_3$ (including NHi radicals) workes to remove NO at the early stage of the reaction: A condition of M_R = [NH$_3$]/[NO+SO$_2$] = 1.5 is equivalent in M_R = [NH$_3$]/[NO] = 3.0. **Figure 6** shows NO removal at [NH$_3$]/[NO] = 3.0 in NO/O$_2$/N$_2$ system and [NH$_3$]/[NO+SO$_2$] = 1.5 in NO/SO$_2$/O$_2$/N$_2$ system. Both characteristics of NO removal showed good agreement. Injected NH$_3$ and NHi radicals are selectively reacted with NO.

The reaction of SO$_2$ removal occurs after the reaction of NO removal, therefore the condition of M_R = [NH$_3$]/[NO+SO$_2$] = 1.5 is equivalent in M_R = [NH$_3$]/[SO$_2$] = 2.0, because a part of NH$_3$ is consumed by NO removal. In fact, SO$_2$ removal in NO/SO$_2$/O$_2$/N$_2$ system at M_R = 1.5 was similar to that in NO/O$_2$/N$_2$ at M_R = 2.0.

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