Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 197 (2008) 50–54

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Optimization of the removal efficiency of nitrogen oxides in the air using a low-pressure Hg lamp

Juyoung Jeong [a], Jongsoo Jurng [a], Sungmin Jin [a], Yundeok Kim [b,*]

[a] *Environment Technology Research Center, Korea Institute of Science and Technology, Hawolgok, 39-1 Sungbuk, Seoul 136-791, Republic of Korea*
[b] *Department of Architecture, Incheon city college, Dowha 235, Namgu, Incheon 402-750, Republic of Korea*

Received 14 June 2007; received in revised form 10 December 2007; accepted 12 December 2007
Available online 23 December 2007

Abstract

The photo-oxidation of gaseous nitrogen oxide (NO_x) by a low-pressure Hg lamp ($UV_{254+185\,nm}$) irradiation was studied. Nitric oxide gas (NO) was rapidly converted to nitrogen dioxide (NO_2) to form nitric acid (HNO_3) by continuous reactions with ozone and hydroxyl radicals which are produced by $UV_{254+185\,nm}$ irradiation. Because HNO_3 is water-soluble, it can easily be removed by water spray. It was found that high removal efficiency of NO_x was recorded at the reaction conditions of humidity above 40% and the reaction temperature below 100 °C. NO_x removal efficiency increases with lower inlet concentration and longer residence time. The conversion of NO_2 to HNO_3 by $UV_{254+185\,nm}$ irradiation was easier than that of NO, which indicates that the pre-oxidation of NO to NO_2 might be effective for enhancing the amount of NO_x removal.

Keywords: Photo-oxidation; NO_x; Ozone; Low-pressure Hg lamp; Hydroxyl radical

1. Introduction

Nitrogen oxides (NO and NO_2) are emitted from automobile exhausts and the combustion of coals and thermal power plants, and cause many environmental problems. NO_x are, for example, responsible for the formation of acid rains and the photochemical pollution results in diseases of the human respiratory system.

The selective catalytic reduction (SCR) process has been widely used to remove NO_x in emission sources such as power plants, waste incinerators, and industrial boilers [1,2]. Recently, non-thermal plasma processing has received much attention as an alternative NO_x removal facility [3–9]. Several attempts have been conducted to use pulsed corona [3–5], electron beam [6], and barrier discharge [7,8] based, non-thermal plasma techniques for simultaneous removal of SO_2 and NO_x from combustion flue gas. However, SCR and the non-thermal plasma process have their own inherent drawbacks. The SCR process requires an expensive catalyst and ammonia. Other problems encountered include secondary pollution by the reducing agent, fouling and loss of expensive catalyst [10]. The major issues in the application of the non-thermal process are the formation of a variety of undesirable byproducts, the difficulties in scale-up to the industrial level, a danger in maintenance such as electrical shock, etc. Therefore, these methods may not be suitable for reduction of NO_x from the ambient environment or some industrial facilities where the emissions are at low level concentrations below 100 ppm. Photocatalytic oxidation (PCO) also has been applied to remove NO_x of ambient level [11–13]. Devahasdin et al. studied PCO of nitric oxide (NO) over TiO_2 catalyst at source levels (5–60 ppm) and reported that the PCO process could remove NO via a series of oxidation by the OH radical: $NO \rightarrow HNO_2 \rightarrow NO_2 \rightarrow HNO_3$ [12]. Wang et al. proposed a process capable of removing NO_x, SO_2 and mercury simultaneously by adding ozone in the flue gas. In the study, he reported that NO could be converted into the water-soluble NO_2^- or NO_3^- by only ozone injection [14].

The present paper deals with photo-oxidation by the direct ultraviolet (UV) irradiation method to remove NO_x in the polluted gas stream. We used an UV lamp to emit wavelengths of 254- and 185-nm ($UV_{254+185\,nm}$), which are capable of simultaneously producing ozone (O_3) and hydroxyl (OH) radicals in the air. Therefore, it is expected that NO_x can be more effectively removed to nitric acid (HNO_3) due to the oxidation with

---

* Corresponding author. Tel.: +82 32 760 8435; fax: +82 32 760 8434.
E-mail address: kimyun@hanmail.net (Y. Kim).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2007.12.004

O_3 and OH radicals than the PCO process. The formed HNO_3 can be easily removed with conventional air pollution control devices such as wet scrubber. This study investigated the characteristics of NO_x removal under a variety of operation parameter conditions.

2. Experimental

A schematic diagram of the lab-scale, experimental setup is shown in Fig. 1. The system consisted of a NO_x gas feeding unit, UV photo-reactor, and NO_x analyzer. Simulated gas was fed into the reactor using mass flow controllers. We chose NO gas as the target pollutant, because it is the typical form discovered in most NO_x emission sources.

NO_2 gas was used to compare the photo-oxidation characteristics with NO gas. NO and NO_2 gases were supplied by high-pressured cylinders. Water vapor was obtained by passing dried air through a bottle containing deionized water at room temperature. The relative humidity from the gas stream was measured in front of the photo-reactor using a humidity measuring instrument (Testo 623, Testo Co. Ltd.).

The cylindrical photoreactor contained a UV lamp located in the center. Irradiation was performed with a low-pressure mercury lamp with a maximum at 254-nm and a smaller (<5%) emission at 185-nm (G12T5VH, Philips Co. Ltd.). The ultraviolet output was 30 $\mu W/cm^2$.

NO_x gas in the effluent gas was monitored with a continuous NO_x analyzer (QUINTOX, Kane-May Co. Ltd.) which reads NO, NO_2 and NO_x ($NO + NO_2$) separately. To quantify the NO photo-oxidation products, the effluent gas was passed through an impinger with deionized water, and the liquor sample obtained was analyzed with ion chromatography (DX-100, Dionex). As UV-induced O_3 can interfere with the measurement of NO_x by the NO_x analyzer, we used an electrical furnace to eliminate such interference. The furnace temperature was set to 400 °C, which is capable of decomposing ozone thermally. A preliminary test showed that there were no changes in concentration observed when both NO and NO_2 were passed in the furnace.

The UV irradiation experiments were started after inlet and outlet NO concentration were equalized (1 h). After the UV lamp was turned on, we investigated the NO and NO_2 concentrations in the effluent gas stream. From the measurements of NO and NO_2, the NO_x removal efficiency were calculated by the following equations, respectively:

$$NO_x \text{ removal efficiency } (\%) = \frac{[NO]_{inlet} - [NO + NO_2]_{outlet}}{[NO]_{inlet}} \times 100 \qquad (1)$$

3. Results and discussion

3.1. Photo-oxidation of NO by $UV_{254+185\,nm}$ irradiation

Fig. 2 shows that NO in the effluent stream was rapidly disappeared with the turn-on of $UV_{254+185\,nm}$ irradiation, while a high concentration of NO_2 was observed. Thereafter, NO_2 concentration was subsequently reduced with increasing irradiation time and then remained stable.

When humid air is irradiated with $UV_{254+185\,nm}$, O_3 and OH radicals can be produced in the air stream via photochemical oxidation of water and oxygen molecules, according to the following reaction mechanism [15,16]:

$$H_2O + h\nu \rightarrow H + OH^\bullet \qquad (2)$$

$$O_2 + h\nu\,(< 243\,nm) \rightarrow O(^1D) + O(^3P) \qquad (3)$$

$$O(^1D) + M \rightarrow O(^3P) + M\,(M = O_2 \text{ or } N_2) \qquad (4)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (5)$$

$$O_3 + h\nu\,(< 310\,nm) \rightarrow O(^1D) + O_2 \qquad (6)$$

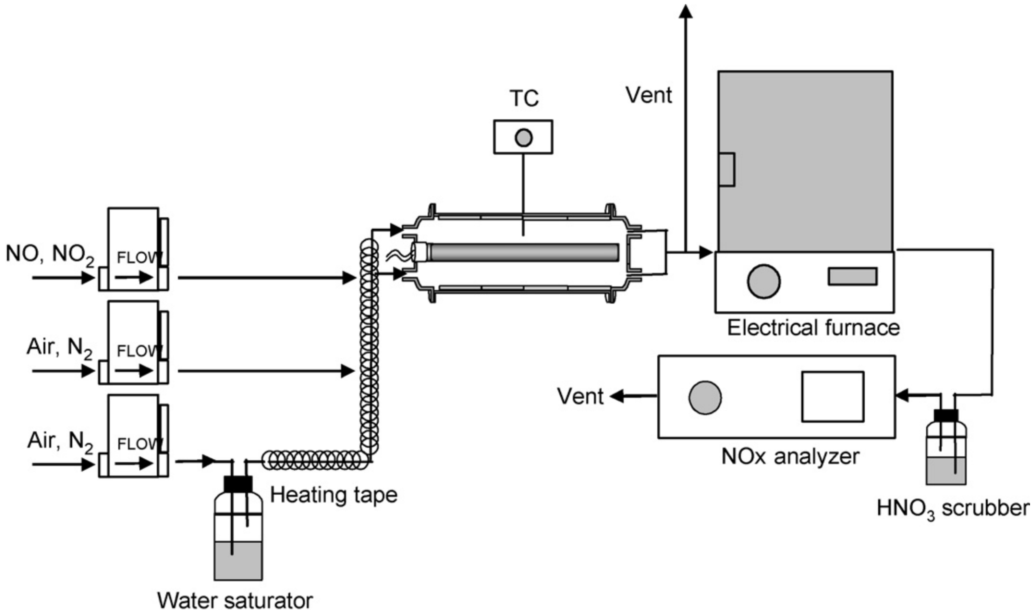

Fig. 1. Schematic diagram of the experimental apparatus.

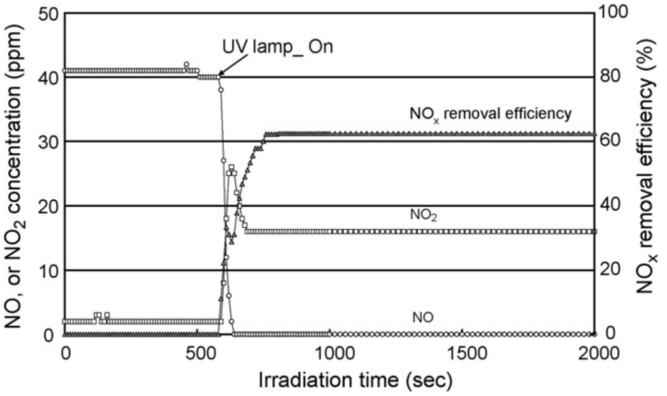

Fig. 2. Time course behavior of NO removal with UV irradiation. Residence time, 12 s; NO concentration, *ca.* 42 ppm; relative humidity, *ca.* 40%; O_2 concentration, 20%; reaction temperature, 25 °C.

Table 1
Generalized NO/NO_2 oxidation mechanisms and rate constants

Reactions	Rate constants
$O_3 + NO \rightarrow NO_2 + O_2$	$k = 2.3 \times 10^{-12} \exp(-1450/T)\ \mathrm{cm^3\ s^{-1}}$
$O + NO + M \rightarrow NO_2 + M$	$k = 5.0 \times 10^{-33} \exp(900/T)\ \mathrm{cm^3\ s^{-1}}$
$NO + HO_2 \rightarrow NO_2 + OH$	$k = 3.7 \times 10^{-12} \exp(240/T)\ \mathrm{cm^3\ s^{-1}}$
$NO + OH + M \rightarrow HNO_2 + M$	$k = 7.4 \times 10^{-31}\ (T/300)^{-2.4}\ \mathrm{cm^6\ s^{-1}}$
$NO_2 + OH + M \rightarrow HNO_3 + M$	$k = 2.6 \times 10^{-30}\ (T/300)^{-2.7}\ \mathrm{cm^6\ s^{-1}}$

$$O(^1D) + H_2O \rightarrow 2OH^{\bullet} \qquad (7)$$

The formed O_3 and OH radicals can participate in oxidizing NO to HNO_3. The generalized reactions relating to NO/NO_2 oxidation process are listed in Table 1 [5,17]. Therefore, it is reasonable to expect that NO reacts rapidly with O_3 to form NO_2, and then that NO_2 is oxidized to HNO_3 in the presence of OH radicals. Fig. 3 shows the ozone concentration formed with and without NO gas feeding. As shown in this figure, the ozone concentration was significantly reduced when the NO was presented. In addition, the disappeared ozone concentration is approximately in accord with the NO feed concentration. This suggests that most of the fed NO reacts with ozone to form NO_2 gas.

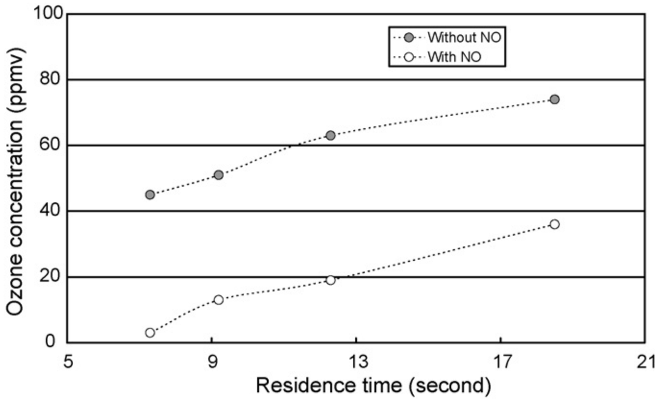

Fig. 3. Ozone concentration formed from UV irradiation with and without NO feeding.

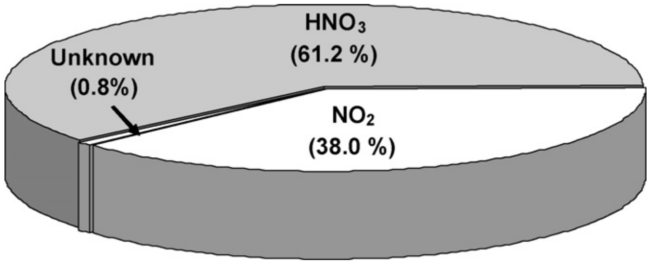

Fig. 4. Mass balance calculated from NO oxidation products analysis. Residence time, 12 s; NO concentration, *ca.* 42 ppm; relative humidity, *ca.* 40%; O_2 concentration, 20%; reaction temperature, 25 °C.

The NO oxidation products in the effluent gas liquor sample were investigated, and mass balance was established as shown in Fig. 4. The result showed that no nitrogen ions were observed except for NO_3^- ion and NO_3^- selectivity reached nearly 60%, which means that the disappeared NO with UV irradiation was mainly converted to HNO_3. Based on the observation, NO_x removal efficiency presented in Fig. 2 implies NO_3^- selectivity. In a previous study, we reported the high NO_3^- selectivity obtained from NO photo-oxidation [18].

Investigating the transient behavior of PCO of NO, Devahasdin et al. [12] reported only 35% NO conversion rate at a residence time of 12 s and inlet NO concentration of 40 ppm, while the final product from NO conversion was mostly NO_2. It should be noted that there was 100% conversion of NO to NO_2 by $UV_{254+185\,nm}$ irradiation at the same residence time and inlet concentration. In addition, the conversion from NO to HNO_3 was much higher than that of PCO.

3.2. Relative humidity effect

The effect of relative humidity (RH) on NO conversion and NO_x removal is shown in Fig. 5. The water concentration ranged from approximately 0 to 80%. The other parameters were kept constant at the base conditions of 42 ppm inlet NO concentration and 12 s residence time. Complete conversion of NO was maintained constantly at all tested RH levels, but total NO_x removal was dependent on RH as seen as Fig. 5. When no water vapor was fed into the reactor, NO_x removal efficiency was as low as

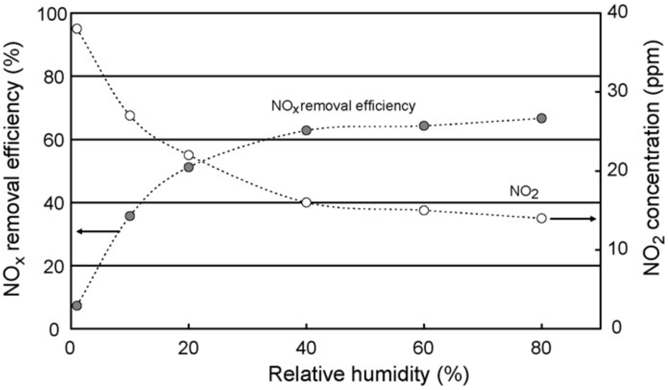

Fig. 5. Effect of relative humidity on the total NO_x removal. Residence time, 12 s; NO concentration, *ca.* 42 ppm; O_2 concentration, 20%; reaction temperature, 25 °C.

10%. In that condition, a large amount of ozone was formed with UV irradiation, but little OH radicals. Therefore, the low NO_x removal efficiency with the low RH was probably caused by the lack of OH radicals capable of oxidizing NO_2. However, the total NO_x removal rate significantly increased with increasing RH in addition of water vapor from 0 to 40%, and remained constant at RH above 40%. Because water vapor is essential to form OH radical in the air, increasing RH enhances the NO_x removal. Meanwhile, the constant NO_x removal efficiency at humidity levels above 40% RH was probably due to the limitations on the UV light available to form OH radicals.

3.3. Inlet concentration effect/residence time effect

The effect of NO inlet concentration on NO conversion and the total NO_x removal is shown in Fig. 6. The results indicated that NO conversion was 100% over the full tested NO concentration range, implying that ozone production was enough to oxidize NO completely in the NO concentration range tested in this study. However, NO_x removal efficiency decreased with increasing inlet concentration. The total NO_x removal efficiency was above 90% at inlet concentration below 20 ppm but was gradually reduced to 37% at 60 ppm. The reduction in total NO_x removal efficiency was due to the increased NO_2 level at higher NO inlet concentration for the same amount of OH radicals.

Fig. 7 indicates the effect of residence time. The NO conversion remained as high as 100% regardless of the change in residence time. However, the total NO_x removal efficiency increased steadily as the residence time increased from 7.3 to 18.5 s, at both 10 and 43 ppm, indicating that reaction rate of NO_2 and OH radicals is strongly dependent on the residence time. It was worthy to note that lower concentration led to higher removal at the same residence time. Therefore, lower inlet NO concentration and longer residence time are favorable to enhance NO_x removal.

3.4. Reaction temperature effect

The effect of reaction temperature on NO conversion and NO_x removal was investigated, as shown in Fig. 8. The NO conversion was 100% regardless of reaction temperature variation, whereas the NO_x removal efficiency increased with increasing reaction temperature until below 100 °C, but decreased again with temperature increase above 100 °C.

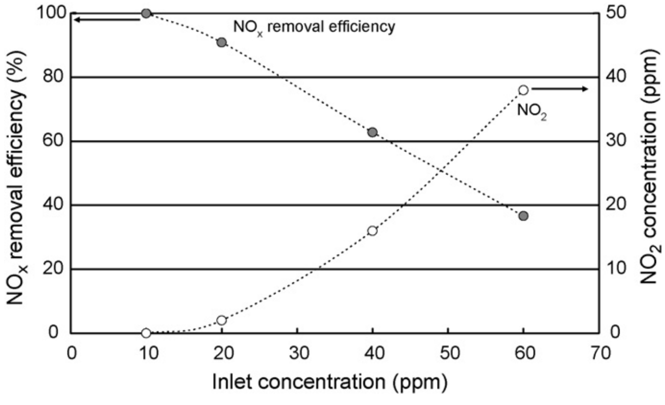

Fig. 6. Effect of inlet NO concentration on total NO_x removal. Residence time, 12 s; relative humidity, ca. 40%; O_2 concentration, 20%; reaction temperature, 25 °C.

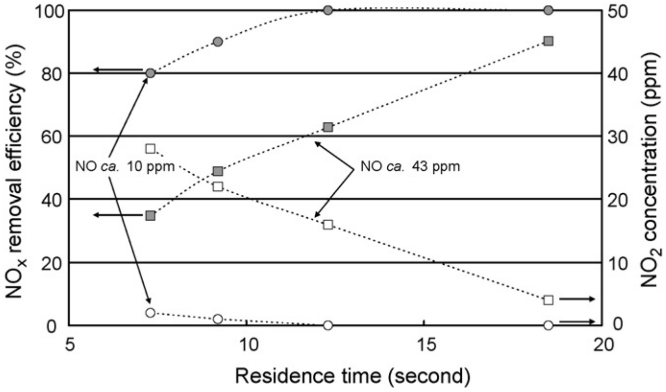

Fig. 7. Effect of residence time. Relative humidity, ca. 40%; O_2 concentration, 20%; reaction temperature, 25 °C. (●) NO_x removal efficiency from ca. 10 ppm NO gas; (○) NO_2 concentration from ca. 10 ppm NO gas; (■) NO_x removal efficiency from ca. 43 ppm NO gas; (□) NO_2 concentration from ca. 43 ppm NO gas.

The increase in the NO_x removal with increasing reaction temperature up to 100 °C was probably due to the increased collision frequency between the reactants and reactive species. Meanwhile, the increase in gas temperature accelerates the velocity of gas in the reactor, which suggests a reduced residence time at the same flow rate. In this experiment, the residence time of 12 s at 25 °C corresponds to the approximately 9.3 s at 100 °C.

Therefore, the reduction tendency of the removal efficiency at above 100 °C was probably due to a reduced residence time. Nevertheless, the result is comparable to the result shown in the residence time effect of Fig. 7. Fig. 7 shows that the NO_x removal efficiency was approximately 49% at a residence time of 9.3 s and 25 °C. However, in Fig. 8, when the temperature was 100 °C, the removal efficiency was 64%, even at the same residence time. This was attributed to the increased collision frequency between the reactants and reactive species, which retarded the decrease in NO_x removal as a result of the shorten residence time.

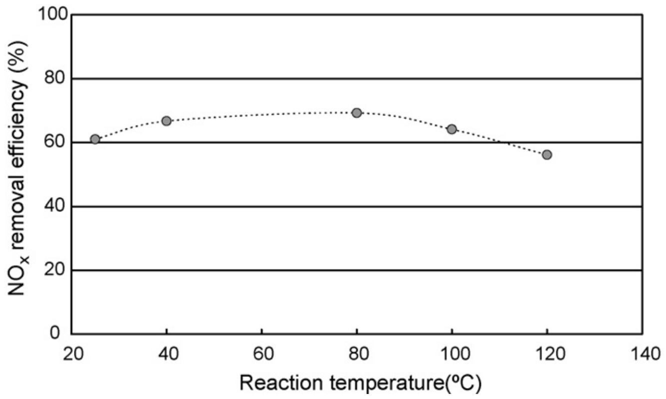

Fig. 8. Removal efficiency of reaction temperature. Residence time, 12 s; relative humidity, ca. 40%; O_2 concentration, 20%; NO concentration, ca. 40 ppm.

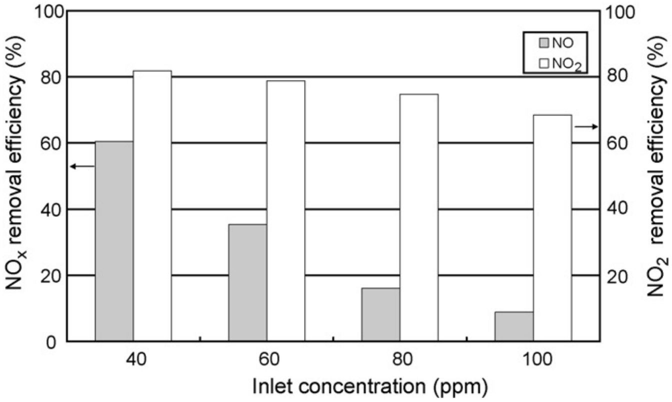

Fig. 9. Comparison of removal efficiencies of NO and NO_2 by the UV irradiation. Residence time, 12 s; relative humidity, *ca.* 40%; O_2 concentration; 20%, reaction temperature, 25 °C.

3.5. *Comparison of photo-oxidation of NO and NO_2 with $UV_{254+185\,nm}$ irradiation*

Photo-oxidations of NO and NO_2 by $UV_{254+185\,nm}$ irradiation were compared at the same experimental conditions. As shown in Fig. 9, NO_x removal efficiency in NO_2 photo-oxidation was much higher than that of NO. In addition, NO_x removal from NO decreased rapidly with increasing inlet concentration, whereas for NO_2, high removal efficiency was obtained even at an inlet concentration of 100 ppm.

In NO photo-oxidation, NO consumes ozone rapidly, producing NO_2. Therefore, the decrease of ozone in the reactor may have caused a reduction of OH radicals by inhibiting their formation according to the mechanism described in Eqs. (5) and (6). In contrast, since NO_2 has low reactivity with ozone, further OH radicals can be formed in the reactor. Therefore, NO_2 could be effectively oxidized to HNO_3 through the attack of the abundantly formed OH radicals.

4. Conclusions

Treatment process for low concentration NO_x using the short-wavelength $UV_{254+185\,nm}$ irradiation was presented. Ozone and hydroxyl radical produced by $UV_{254+185\,nm}$ irradiation effectively converted NO to the water-soluble and easily removable nitric acid by water spray. NO_x removal efficiency was high at the humidity above 40% and reaction temperature below 100 °C. It was clear that lower inlet concentration and longer residence time were favorable for NO removal. Conversion of NO_2 to HNO_3 by $UV_{254+185\,nm}$ irradiation was easier than that of NO, indicating that pre-oxidation of NO to NO_2 may be effective for enhancing NO_x removal.

Acknowledgment

This work was supported by Eco-Technopia 21 Project (013-071-062) of Korea.

References

[1] L. Lietti, Appl. Catal. B: Environ. 10 (1996) 281–297.
[2] M. Radojevic, Environ. Pollut. 102 (1998) 685–689.
[3] R. Gasparik, N. Mine, S. Ihara, S. Satoh, C. Yamabe, Vacuum 59 (2000) 220–227.
[4] T. Fujii, M. Rea, J. Electr. 51 (2001) 8–14.
[5] H. Lin, X. Gao, Z. Luo, K. Cen, Z. Huang, Fuel 83 (2004) 1349–1355.
[6] M.T. Radoiu, D.I. Martin, I. Calinescu, J. Hazard. Mater. 97 (2003) 145–158.
[7] M.B. Chang, S.C. Yang, AIChE J. 47 (2001) 1226–1233.
[8] K.P. Francke, H. Miessner, R. Rudolph, Catal. Today 59 (2000) 411–416.
[9] J.O. Chae, J. Electr. 57 (2003) 251–262.
[10] X. Hu, J. Zhang, S. Mukhnahallipatna, J. Hamann, M.J. Biggs, P. Agarwal, Fuel 82 (2003) 1675–1684.
[11] H. Ichiura, T. Kitaoka, H. Tanaka, Chemosphere 51 (2003) 855–860.
[12] S. Devahasdin, C. Fan, K. Li, D.H. Chen, J. Photochem. Photobiol. A: Chem. 156 (2003) 161–170.
[13] S. Matsuda, H. Hatano, Powder Technol. 151 (2005) 61–67.
[14] Z. Wang, J. Zhou, Y. Zhu, Z. Wen, J. Liu, K. Cen, Fuel Process. Technol. 88 (2007) 817–823.
[15] J.Y. Jeong, K. Sekiguchi, K. Sakamoto, Chemosphere 57 (2004) 663–671.
[16] J.Y. Jeong, K. Sekiguchi, W.G. Lee, K. Sakamoto, J. Photochem. Photobiol. A: Chem. 169 (2005) 279–287.
[17] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics, John Wiley & Sons, 1986.
[18] J.Y. Jeong, K. Sekiguchi, M. Saito, Y.G. Lee, Y.D. Kim, K. Sakamoto, Chem. Eng. J. 118 (2006) 127–130.