

Examination of the Optimized Conditions for the Conversion of NO_x Pollution in DBD Plasma Reactor

Yarahmadi, Rasoul*⁺

Department of Occupational Health, Faculty of Public Health, Iran University of Medical Sciences, Tehran, I.R. IRAN

Mortazavi, Sayed Bagher

Department of Occupational Health, Faculty of Medical Science, Tarbiat Modares University, Tehran, I.R. IRAN

Omidkhah, Mohammad Reza

Department of Chemical Engineering, Faculty of Engineering, Tarbiat Modares University, Tehran, I.R. IRAN

Asilyan, Hassan

Department of Occupational Health, Faculty of Medical Science, Tarbiat Modares University, Tehran, I.R. IRAN

Moridi, Parvin

HSE-Department, Iran Medical Science (irmed), Tehran, I.R. IRAN

ABSTRACT: Since NO_x family, one of the most important causes of air pollution, is the primary source of acid rains, ozone layer depletion, and breathing disorders, mitigation of these pollutants is now a global concern. In the off-gases of internal combustion engines running with oxygen excess, non-thermal plasmas (NTPs) have an oxidative potential, which results in an effective conversion of NO to NO₂. This paper aims at studying the methods of mitigating and eliminating NO_x in an atmospheric and non-thermal condition by means of plasma reactors. It examines some key parameters such as temperature, space velocity, voltage, and propane/NO_x mole ratio. The results showed that, the space velocity in the 11500-2300 h⁻¹ domain did not show any significant results on the NO_x conversion. Our findings also revealed that the optimal conditions for conversion of NO into N₂, O₂, and NO₂ are temperature (180 °C), voltage (10 kV), and equal mole ratio of propane in NO_x. In this condition, the optimal conversion efficiency of 78% and the standard deviation of 12% were obtained. The optimal temperature, voltage, and the mole ratio of propane in NO_x conversion to N₂ and O₂. (efficiency=53%) are 180°C, 5 kV, and 0.3 respectively. Plasma reactor acts as primery treatment in the direct mitigation of NO_x into neutral and non-poisonous molecules of O₂ and N₂.

KEY WORDS: NO_x removal, Non-thermal plasma, Corona, Dielectric barrier discharge.

* To whom correspondence should be addressed.

+ E-mail: rasoulpch@yahoo.com

1021-9986/10/1/133

8/\$/2.80

INTRODUCTION

Driven by world-wide emission regulations, there is a need for the removal of nitrogen oxides in engine exhaust gases with oxygen excess (lean-burn and diesel engines) in a wide range of engine operation conditions.

Nowadays, the technical application of plasma is expanding rapidly and this expansion is closely related to the outstanding or better to say unique characteristics of plasma technology [1, 2, 3].

There are, on the other hand, investigations for about 10 years now to reduce the NO_x emissions by a non-thermal plasma (NTP) in the gas phase.

High-energetic electrons generated usually in a corona discharge or a dielectric barrier discharge react with the molecules in the gas phase producing reactive species (radicals, excited molecules) that undergo further reactions. The plasma energy is deposited into the electrons, rather than to ions or molecules leaving the gas mixture essentially at the temperature of the environment (cold plasma).

The main objectives of this paper are identification, modification and optimization of physical and chemical parameters for the optimal mitigation of contamination of NO_x in exhaust gases. The emission of the gaseous contaminants in the environment in great amounts has brought about terrible effects on humans, soil, and water. Moreover, commitment to the national and international obligations, treaties, protocols, conventions, and resolutions aimed at reducing the emission of contaminants has multiplied the importance of controlling NO_x as the second atmospheric pollutant after the airborne particles. The main NO_x contamination controlling techniques include selective, non-selective, and chemical reductions and plasma-aided reduction. In fact, plasma technology due to the simplicity of treatment process, low cost of designing, manufacturing, maintenance, and its independence from the chemical and mechanical equipments has got special significance [4-8]. The advantages of this process are an increase in the interaction potentialities and a natural fusion of the contaminants and influential factors on the conversion system. In addition, in order to control the factors affecting the plasma reactor, the velocity of the air flow is selected proportionate to the diameter of the reactor in such a way that the opportunity for the composition of molecules and active radicals through enough space time

is provided. Some other advantages of non-thermal plasma are its mitigation performance potentiality in spreading resource matrix especially in oil and gas industries as well as in petrochemical complexes [9].

The gas velocity control and space time of the exhaust gas from the fixed and removable resources in mixing and completing the final reaction of the plasma treatment are so influential that it is possible to use this potentiality by minimum cost and considering all the technical and economical aspects. Due to the technical considerations in designing the geometric structure of the plasma reactor, two key factors of pressure drop and dead volume as affective factors in reducing the treatment of output are surely minimized [10-12]. One of the by-products of this process is Ozone as an unwanted combination which is partially controlled by some dielectric barriers and regulating the oxygen concentration. Hence, the identification and specification of the factors affecting NO_x treatment and studying the mutual effects of the influential factors on the response variable of NO_x conversion coefficient by the optimization approach in the laboratory conditions are among the main objectives of this study [13-14].

EXPERIMENTAL ARRANGMENT AND METHOD

For laboratory experiments, the NTP was obtained in a coaxial reactor by dielectric barrier discharges, using a glass or a ceramic tube as a dielectric barrier (160 mm high, 11 mm Dia, 1.1 mm thickness) between the inner high voltage electrode (180 mm long and 14 mm Dia thin justen wire 98.5%) and a grounded electrode on the outer wall. The gas discharges were excited by application of a high-voltage pulse generator (ca. 20 kV, 5 ma, with sensitivity .01 ma) (Fig. 1).

In this experiment, the discharge mechanism with dielectric barriers in the non-thermal plasma process under the atmospheric conditions and the temperature of 100-180°C has been used.

The entering temperature of the plasma reactor was first measured by some thermal sensors with an accuracy of 0.1°C and then it was sent to the furnace thermal monitoring of the system. The air flow containing NO_x contaminants was injected into the thermal furnace for the thermal balance up to 180°C and then it was injected on the reactor. The thermal rate of the furnace is set to 10°C/min by the thermocouple system.

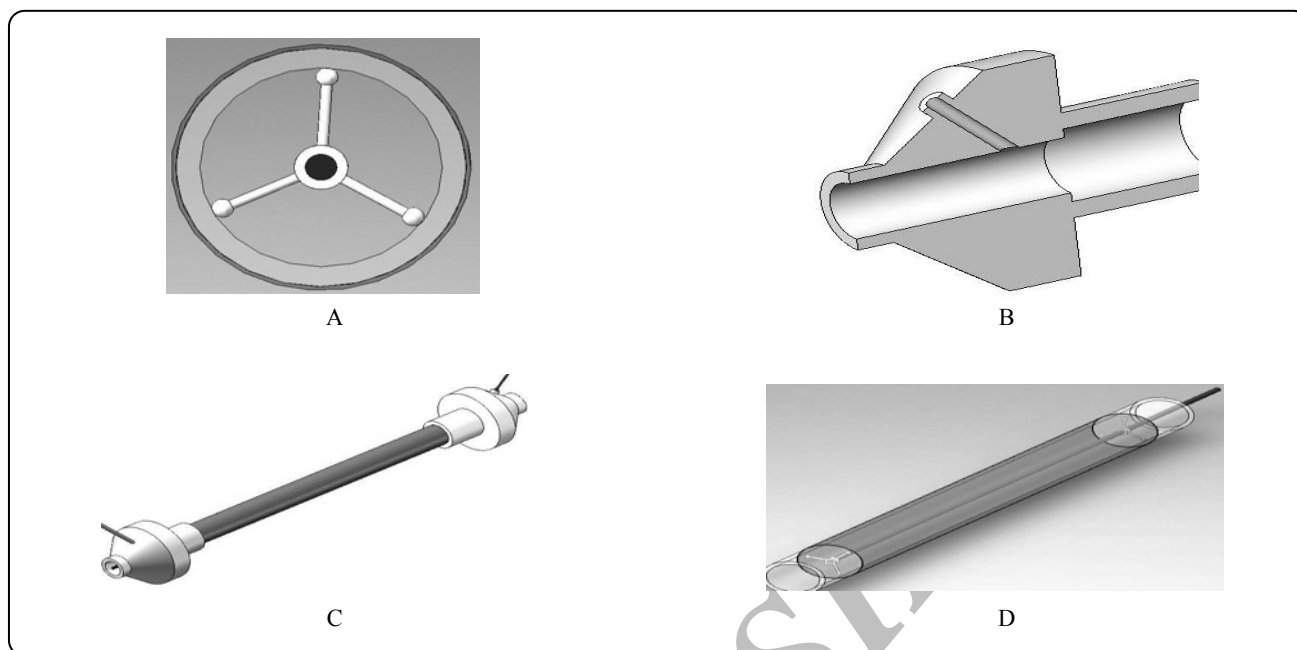


Fig. 1: Schematic of the plasma reactor. (A) Cathode spacer, (B) DBD and anode holder, (C) main body of plasma reactor, (D) view of anode surface.

The system was feeded by mixture subjected in N_2 (90%): O_2 (5%): C_3H_8 (30-100ppm): H_2O (5%):

NO_x (100ppm). The amount of input air volume was regulated by Mass Flow (Model M-W Instrument SN 3605) Controller and then conducted to the mixture and thermal units. At first a two-level factorial design by the help of potentially influential factors, i.e. temperature, mole ratio of propane gas, space velocity and consumed voltage was utilized ($2^4=16$ test). The experiments were then carried out on three major factors, temperature, voltage, and mole ratio of propane gas, in three factorial levels ($3^3=27$ test) to obtain some more accurate findings and a higher level of significance. In two different stages and on the basis of the specifications of the two experimental designs, 43 samples were carefully examined to determine the optimal condition of each factor. The main aim of this method was to obtain logical and accurate information and results through a practical experimental design. With the quantified evaluation objectives, an instant analysis of the sampling points was carried out by real-time approach (MRU Air, Industrial Varioplus instrument, German). In the other method, with quantitative, and qualitative objectives and through some Grap samples accumulated in the glass containers, all unwanted by-products were analyzed. This analysis was carried out by means of mass spectrometric (GC-Mass) or

flame ionization (GC-FID) Detection. Schematic presentation of the equipment is given in Fig. 2.

The mole volume of each gas molecule in STP condition was computed according to the Eq. (1).

$$V_1 = V_2 \times \frac{p_a}{760} \times \left(\frac{273.15}{273.15 + t} \right) \quad (1)$$

Where, V_2 = mole volume of the gas in the measured conditions (t, Pa) in liter,

V_1 = mole volume of the gas in STP condition (273.15K, 760 mmHg) in liter.

The computations related to conversion coefficient of NO were carried out according to the following formula:

$$NO \text{ Conversion}(\%) = \frac{NO_{,IN} - NO_{,OUT}}{NO_{,in}} \times 100 \quad (2)$$

The conversion coefficient of NO_x to other products except NO_x can be worked out from the following formula:

$$NO_x \% = \frac{NO_{X,IN} - NO_{X,OUT} - N_2O_{out}}{NO_{X,in}} \times 100 \quad (3)$$

For mass balance, before and after the plasma reactor, all the concentrations (ppmv) were changed into the mass density. Also in this study compressible behavior of air mixture was evaluated [15-17].

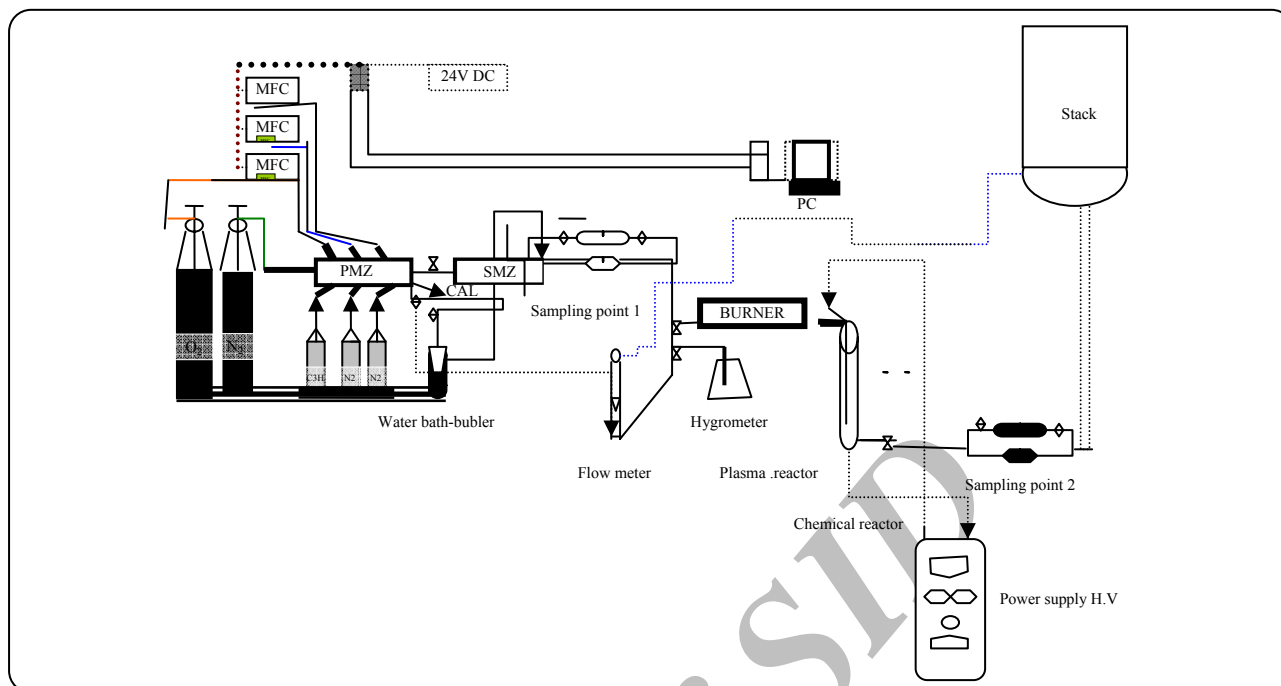


Fig. 2: Schematic of the experimental setup.

The results of the previous studies indicated that the amount of humidity and oxygen in non-thermal plasma process is usually, in a constant limit, influential in the conversion of the NO_x contamination. [18-19].

In the present study we used a five-liter-per-minute (SLPM) flow rate with 100 ppm NO_x concentration. The data analysis was carried out with SPSS software (version 11) and Minitab 14. The interaction effects of the fixed factors on the response variable and the experimental design were carried out by means of two-way ANOVA.

RESULTS AND DISCUSSION

In this study, the interaction effects of four important factors on NO contamination conversion were simultaneously examined. The experiments at two levels for surely specifying the domain of each factor showed that voltage, temperature, and mole ratio of propane affect the conversion of NO and NO_x in the examined domains while space velocity did not show any considerable influence on the process of NO_x conversion (Table 1).

According to the research method, with a certainty of more than 95% and significance level of less than 0.05 was carried out on the conversion of NO_x (NO , NO_x) as

the response variable. In all the experiments in two levels, temperature of $100\text{-}180^\circ\text{C}$, space velocity of $11500\text{-}23000\text{h}^{-1}$, voltage of $5\text{-}10\text{ kV}$, and propane / NO_x mole ratio of $0.5\text{-}1$ were selected and set.

The results presented in Table 1 indicate that temperature, voltage, and the reducer gas factors significantly affected the conversion of NO ($P \leq 0.05$). However, space velocity of $11500\text{-}23000\text{ h}^{-1}$ did not significantly affect the contamination conversion of NO_x ($P \geq 0.05$) whereas space velocity showed a meaningful influence on NO_x conversion in the second objective of the research ($P = 0.003$).

The results of the analysis of the main and compound factors in three levels of the factorial design (Table 2) showed that temperature, voltage, and mole ratio of propane as the main factors significantly affected NO conversion ($P \leq 0.05$).

The results of the experiments (Table 3) showed that the optimal temperature condition in NO_x and NO conversion was 180°C , while the voltage and mole ratio of the reducer gas were different in this process. In addition, compared to the conversion coefficient of NO_x , that of NO had more potential. Also, in 180°C , 10 kV , and equal ratio of propane and NO_x , the conversion coefficient ≥ 0.7 for NO was obtained (Figs. 3 and 4).

Table 1: Results of fix factors effects (two level factorial) in NO_x conversion.

(x-Conversion NO)				(X-Conversion NO _x)	
Factors	Range	Removal %	P _{value}	P _{value}	Removal %
Temperature (°C)	180	0.74	0.04	0.156	0.05
	100	0.65			0.24
Space velocity(h ⁻¹)	2300	0.69	0.763	0.003	0.08
	11500	0.7			0.4
Voltage (kV)	10	0.82	0.001	0.506	0.13
	5	0.56			0.2
C ₃ H ₈ /NO _x Mole ratio	1	0.74	0.027	0.27	0.22
	0.5	0.65			0.1

Table 2: Results of fix factors effects (three level factorial) in NO_x conversion.

(x-Conversion NO)				(X-Conversion NO _x)	
Factors	Range	Removal %	P	P	Removal %
Temperature (°C)	180	0.71	0.0001	0.085	0.46
	140	0.35			0.41
	100	0.49			0.26
Voltage (kV)	10	0.64	0.039	0.67	0.39
	7	0.44			0.41
	5	0.47			0.33
C ₃ H ₈ /NO _x Mole ratio	1	0.59	0.098	0.15	0.45
	0.5	0.5			0.28
	0.3	0.53			0.4

Table 3: Results of factors effects on NO_x conversion optimization.

Measure	(x-Conversion NO)			(X-Conversion NO _x)		
	C ₃ H ₈ /NO _x Mole ratio	Voltage (KV)	Tempe. (°C)	C ₃ H ₈ /NO _x Mole ratio	Voltage (kV)	Tempe. (°C)
Range	0.3	5	180	1	10	180
Average conversion%	0.78			0.53		

NO_x conversion process started at corona threshold limit (5.5kV) and then by the voltage increase, in 7 kV, reached the utmost conversion coefficient of 41% (Fig. 4).

Fig. 5 shows the development of conversion production coefficient of NO and NO_x. At the same time, in the experimental settings compared to the conversion coefficient of NO_x, conversion coefficient of NO has constantly been at a higher level.

The analysis of the obtained results from the conversion of NO gas in the experiments revealed that the optimal conditions for the conversion of NO to N₂, O₂, and NO₂ are: temperature of 180°C, voltage of 10 kV, and an equal propane/NO_x ratio (X-conversion=0.78). However, the optimal condition for the conversion and treatment of NO_x in 180°C shows that the propane/NO_x mole ratio with the voltage of 5 kV equals 0.3 (X-conversion=0.53).

The mean NO_x mitigation in United States, China, Romania, Italy and Japan ranged from 30% to 80% conversion (Penerant B.M. et al., 1990; Zhu A. et al.,

2005; Ighigeanu D. et al., 2005; Kaspar K. et al., 2003; Jinhai N. et al., 2005). A comparison of our findings regarding such factors as temperature range and type of supplied current without a pulse generator in plasma reactor, showed that the mean conversion of NO_x in the present study (NO-Conversion=78%; NO_x-Conversion =53%) turned out to be different from those of other studies carried out in other countries.

The trends of the factors affecting NO_x conversion in four levels were predicted. The results indicated that due to the conversion of NO₂ into NO, and burning of the reducer hydrocarbon, the temperature factor in a range above 180 °C led to the reduction of NO_x conversion (Fig. 6). Increasing the voltage stimulates NO, O₂ and N₂ molecules leading to the formation of N₂O.

This phenomenon directly results in an increase in the conversion of NO and a decrease in the conversion of NO_x (Fig. 7). Increasing the consumption of reducer gas is, in turn, accompanied by the formation of nitride and nitrite ions (Fig. 8) [20].

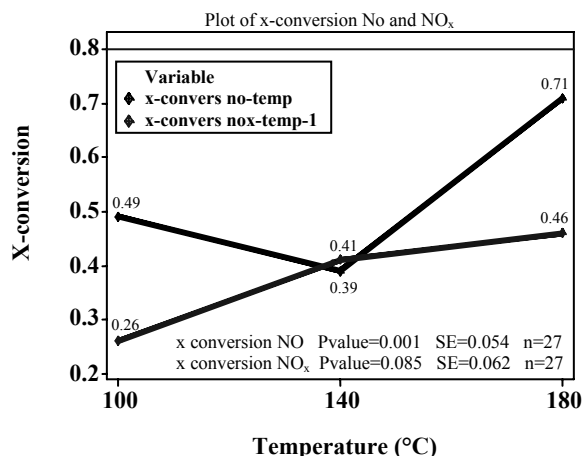


Fig. 3: Trend of temperature effect on NO and NO_x conversion in plasma reactor.

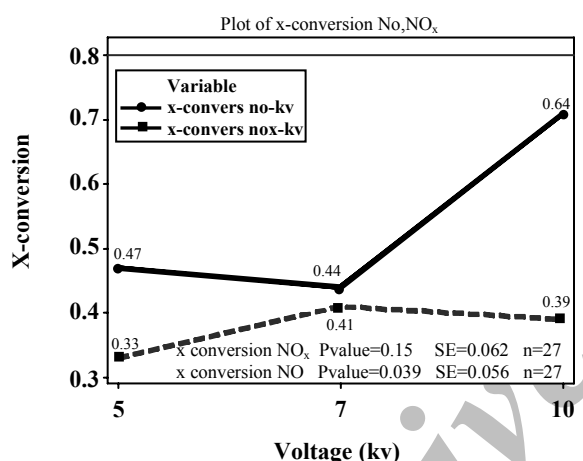


Fig. 4: Trend of voltage effect on NO and NO_x conversion in plasma reactor.

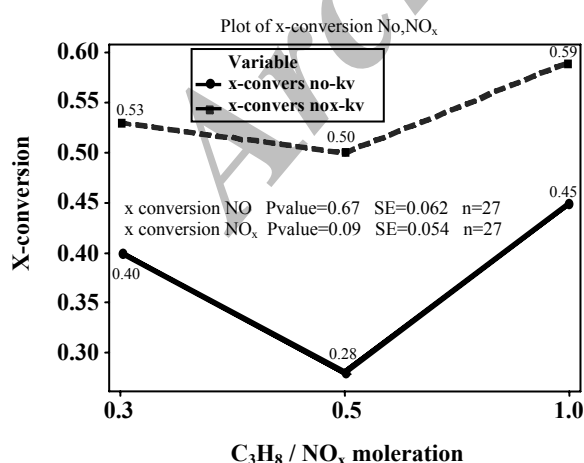


Fig. 5: Trend of propane/NO_x mole ratio effect on NO and NO_x conversion in plasma reactor.

CONCLUSIONS

This study measured the interaction effects of four fixed factors so that an optimized condition for NO_x conversion might be obtained, but in some other countries similar experiments have been carried out at high temperature and by the use of ammonia or other hydrocarbons.

It can be concluded that the above-mentioned factors have provided the optimal conditions for the conversion and mitigation of NO and NO_x contaminants at a significant level. The significant differences in Tables 3 and 4 and Figs. 3 and 4 clearly demonstrate this fact ($p \leq 0.05$). Also, because of the high stability and two-stage nature of the oxidation and reduction processes in NO_x conversion, the utmost conversion coefficient index, under the temperature condition (Table 3), meaningfully amounted to 0.53. Because of the dependence of the space velocity factor on the temperature condition and its low effect on NO conversion, it was omitted in the final tests of this study.

It has been shown that NTPs based on DBD can be used in atmospheric condition and in the presence of reducer gas of propane. It acts with the conversion coefficient of 78%. The direct conversion of NO_x to N₂ and O₂ in plasma reactor was conducted with the lower conversion coefficient due to need for the two simultaneous reactions of oxidation and reduction and different required space time between NO and NO₂ in the limited volume of the plasma reactor.

Because of the low degree of conversion coefficient of NO_x in the output of plasma reactor (NO_x-conversion=0.53), a medium with selective catalysts (zeolith or chemical washing) can be used to complete the exiting NO_x of the reactor.

The main conclusion from this study is the minimum use of equipment, materials, and mechanical tools in the design and production of the DBD reactor, which results in the production of non-poisonous gases (N₂, O₂, CO₂ and H₂O) by minimum energy consumption, this technique can be named as environmentally clean technology.

Acknowledgment

We hereby wholeheartedly appreciate the sincere assistance and collaboration of Mr. Soleimani the head of the Occupational Health Laboratory of Faculty of Medical Sciences, Tarbiat Modares University, Mr. Adilnejad, managing director of Emam Khomani Petrochemical Complex, and respectful staff of the Production Engineering of the Complex.

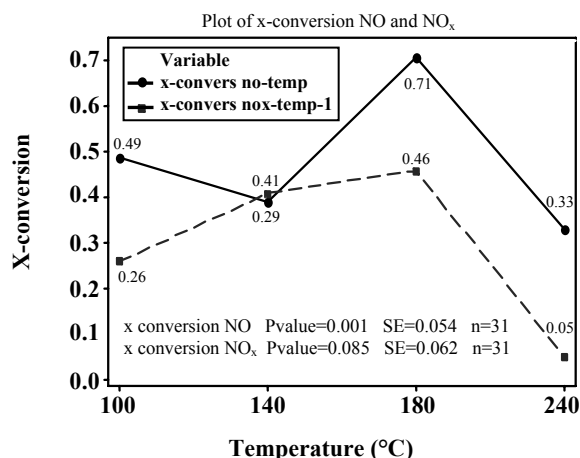


Fig. 6: Trend of temperature effect up to 240°C on NO and NO_x conversion in plasma reactor.

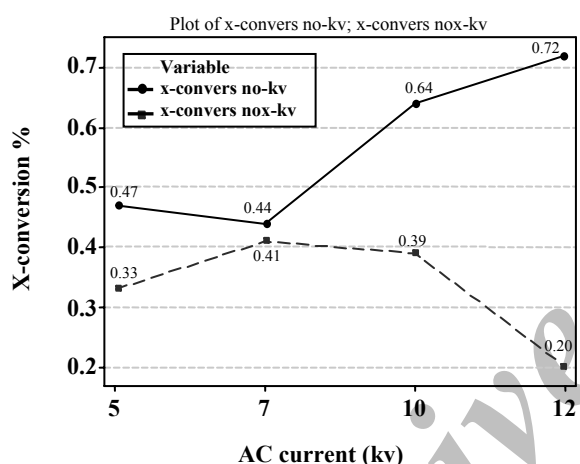


Fig. 7: Trend of voltage effect up to 12 kV on NO and NO_x conversion in plasma reactor.

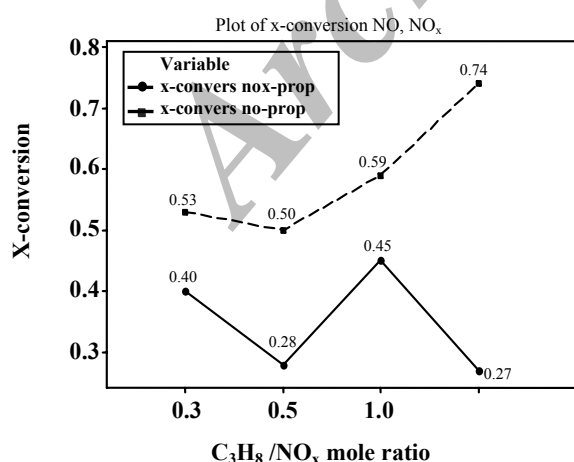


Fig. 8: Trend of propane/NO_x mole ratio effect up to 1.5 on NO and NO_x conversion in plasma reactor.

Received : Dec. 9, 2007 ; Accepted : Jun. 9, 2009

REFERENCES

- [1] Meyer A., Becker A., Design of an UHV Reactor System for Plasma Surface Treatment of Polymer Materials, *Surface and Coatings Technology*, **116-119**, p. 1006 (1999).
- [2] Chang TC., Plasma Surface Treatment In Composites Manufacturing, *Industrial Technology*, **15**, p. 1 (1999).
- [3] Miessner H., Rudolph R., Hammerb R., NO_x Removal in Excess Oxygen by Plasma-Enhanced Selective Catalytic Reduction, *Catalysis Today*, **75**, p. 325 (2002).
- [4] Gui-Bing Ovid A., Radosz M., Nonthermal Plasma Reactions of Dilute Nitrogen Oxide Mixtures, *Ind. Eng. Chem.*, **43**, p. 2315 (2004).
- [5] Europe ECF., Convention on Long-range Transboundary Air Pollution, *Economic Commission*, p. 8 (2007).
- [6] Quality IDEMO, Technical Support Document (TSD) for a Minor Source Operating Permit Renewal, *Operating Permit Renewal* **6**, p. 1 (2000).
- [7] Ighigeanua D., Martina D., Zissulescub E., Macarieb R., Oproiua C., SO₂ and NO_x Removal by Electron Beam and Electrical Discharge Induced Non-Thermal Plasmas, **77**, pp. 493-500 (2005).
- [8] Chae J-O., Non-Thermal Plasma for Diesel Exhaust Treatment, *Journal of Electrostatics*, **27**, p. 251 (2003).
- [9] Nam Shin, DJae Won. H., Detection of OH(A₂S⁺) and O(1D) Emission Spectrum Generated in a Pulsed Corona Plasma, *Bull Korean Chem Soc*, **21**, p. 228 (2000).
- [10] Nozaki K., Ultrashort Pulsed Barrier Discharges and Applications, *Pure Appl. Chem*, **74**, p. 447 (2002).
- [11] V Likhanskii A., Macheret S.O., Optimization of Dielectric Barrier Discharge Plasma Actuators Driven By Repetitive Nanosecond Pulses, 45th AIAA Aerospace Sciences Meeting and Exhibit (2007).
- [12] Mehul P., Patel TTN., "Scaling Effects of An Aerodynamic Plasma Actuator", 45th AIAA Aerospace Sciences Meeting and Exhibit (2007).
- [13] Rusanov V.D., Theoretical Basis of Non-Equilibrium Near Atmospheric Pressure Plasma Chemistry, *Pure & Appl Chem*, **66**, p. 1267 (1994).

- [14] Van Veldhuizen E.M., Corona discharges, fundamentals and diagnostics, "Proc XVI Int Conf", paper C48, (2006).
- [15] <http://www.aus-etute.com.au/index.html>,(2007).
- [16] <http://www.grc.nasa.gov/airplane/mach.html>.mach clenn research center., (2007).
- [17] Jinhai NiuAimin Z., Lingling S., Yong Xu B, "Plasma-Assisted Selective Catalytic Reduction of NO_x by C₂H₂ over Co-HZSM-5 Catalyst Communications, Volume 7(5), P.P. 297-301(2006).
- [18] Dors XY., "Optimisation of Streamer Pulse Repetition Rate in a Corona Discharge Used for NO_x Removal, in Center of Plasma and Laser Engineering, Polish Academy of Sciences, p. 1 (2005).
- [19] Jan Kašpar PF., Hickey H., Automotive Catalytic Converters, *Catalysis Today*, **77**, p. 419 (2003).
- [20] Hassouni K., "Consequences of Soot Particle on the Plasma Remediation of NO_x in the Presence of Hydrocarbons", Engineering, University of Illinois (2000).

Archive of SID