J. KOSAE Vol. 17, No. E 3 (2001) pp. 91 ~ 99
Journal of Korean Society for Atmospheric Environment

# A Study on Production of Nitrogen Oxides in Plasma Reactors

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(Received 2 June 2001; accepted 31 October 2001)

## Abstract

Plasma reactor was used to generate a high potential difference between two surfaces of concentric pyrex tubes by electrical current. The annular gap of the reactor was calculated by trial and error from the breakdown voltage equation and set at 0.45 cm. The overall objective of this research was to know the effects of the frequency, humidity, and residence time on the formation of nitrogen oxides in a plasma reactor. The primary voltage varied from 50 to 90 volts and the frequency was varied in increments of 10 Hz from 60 to 650 Hz at the primary voltage of 90. The increase in the secondary voltage was not linear but exponential at high frequencies. At a maximum concentration of about 745 ppm, the frequency and secondary voltage was 600 Hz and 4,200 volts, respectively.

All tests for the effects of humidity on $NO_x$ production were performed at the optimal setting of 90 volts and 600 Hz frequency. Since the $NO_x$ production was not an one dimensional phenomenon, competing reactions were assumed to occur in the discharge chamber. The sharp peak concentration of 1,810 ppm was observed at 38% of relative humidity. The enhanced production was choked off, and the production rate rapidly dropped to 3 ppm at above 40% of relative humidity. It is assumed that the corona attacks the most vulnerable molecules in the reaction chamber before attacking other more tightly bonded molecules, possibly at humidities above 38% and the optimized 90 volt setting. Thus, there was not enough energy left after attacking all water molecules to decompose an appreciable amount of $N_2$. If nitrogen breakdown does not occur, then oxides of nitrogen are not likely to be produced.

**Key words** : Plasma, $NO_x$ production, Corona, Relative humidity, Frequency

## 1. INTRODUCTION

The use of plasma reactors is an efficient technique to obtain corona which is defined as a purple haze observed on incomplete breakdown of gas when a high voltage potential is applied across a medium containing the gas. Plasma reactors are used to generate a high potential difference between two surfaces of concentric tubes by electrical current. The high voltage drop causes an electrical breakdown of the gas entrapped in the annulus of concentric tubes. The electrical breakdown as discharge is usually initiated due to the presence of free electrons in the gas (Boeing, 1982). These free electrons are drawn to the positively charged surface at high speed. In the process they collide with the gas molecules which are moving at random in the annular space of the reactor to form radical ions and more electrons which recombine to form different kinds of neutral species. On application of a high energy electric

field some free electrons are accelerated to the positive electrodes and collide with the molecules in the fields. Some of these collisions are elastic and others are not, but eventually some of these electrons acquire high kinetic energy. When those electrons strike molecules they knock out other electrons in the outermost orbital and generate ions, radicals, and more free electrons. The radicals and ions formed recombine to form molecules of different or similar characteristics (Coffman and Browne, 1965).

The interest in corona as a reaction energy has grown recently because of its ability to form radicals and the availability of electricity in abundance.

It is also important to understand the basic nitrogen oxide chemistry and the reaction mechanism. Oxides of nitrogen, commonly referred to as $NO_x$, exhibit a peculiar behavior due to the electronic configuration of the nitrogen atom. Nitrogen has the ability to form single, double, and triple covalent bonds. The primary reactions in the plasma have been hypothesized to be as follows (Boeing, 1982).

$$N_2 + e^- \rightarrow N + N + e^-$$
$$O_2 + e^- \rightarrow O_2^- \rightarrow O + O^-$$
$$O + e^- \rightarrow O^+ + 2e^-$$
$$N + O^+ \rightarrow NO^+$$
$$NO^+ + e^- \rightarrow NO$$
$$NO^+ + O^- \rightarrow NO_2$$

The above reaction mechanisms have been suggested to occur in plasma where the driving force for the reactions is the electronic collision of the molecules and electrons in the electric field. These molecular collisions result in the formation of free radicals and ions which create an avalanche of the charged particles. Since the initial concentration of the electrons is low, the initial collisions result in the excitation of the molecules and are responsible for the emission of light and the formation of metastable molecules. These excited and metastable species are ionized to form other ions and radicals.

Based on the above reaction mechanisms, an overall objective of this research was to expand on the results obtained during the previous study (Lim and Yoo, 1993) and to know the effects of the frequency, humidity, and residence time on the formation of nitrogen oxides in the plasma reactor. The variables that needed to be monitored for this research were primary voltage, frequency, residence time, humidity, and power input.

The production conditions of $NO_x$ could be applied to prove in more details the destruction mechanism of $NO_x$ by plasma and to use in the design for a alternating current plasma reactor (ACPR).

## 2. EXPERIMENT

### 2. 1 Experimental apparatus

A plasma reactor is the primary tool for this research and it consists of two concentric pyrex tube which is fused at both ends as shown in Fig. 1. This gives an annular space for the flow of gas through it. Early studies (Coffman and Browne, 1965) have proved that an electrical field in concentric cylinders on reactor geometry initiates a breakdown at lower voltages than in flat plates.

The annular gap of the reactor was calculated by trial and error from the breakdown voltage equation (Dibelius *et al.*, 1964) and set at 0.45 cm, since the maximum rating of the secondary voltage of the transformer was 15,000 V (designed to 18,000 V). The discharge reactor was fabricated using Pyrex glass which was chemical resistant borosilicate glass with a dielectric constant of 4.6 at 25°C.

The electrical circuit consists of a transformer (specially designed. primary 120 V, 60 Hz, Secondary 18,000 V, Mid point grounded, Korea), a generator (B.K. PRECISION, 3011B), power source high voltage probes (John Fluke, 80K40), an watt meter (GE, 3720341, type p-3, single phase) and a multimeter (John Fluke Mfg. Co. 8050A) connected to measure the voltage, current and the power. A hygrometer/thermometer (Davis Instrumentation, DTH1) was connected in line to monitor the humidity of the gas. The magnitude of the primary voltage was varied by changing

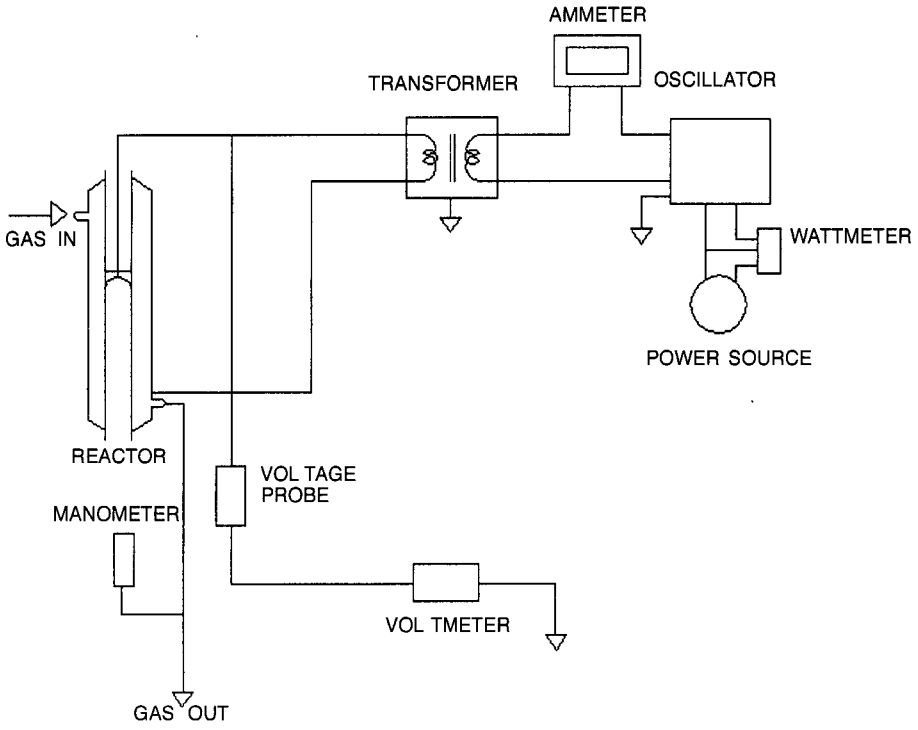


**Fig. 1. Schematic of plasma reactor system.**

the amplitude of the input AC. The secondary voltage was varied by changing the frequency of the current into the primary of the transformer. The transformer is grounded at a mid point. This implies that the secondary voltage is twice the measured voltage on the multimeter connected to one end of the secondary coil. The flow of air was regulated using a mass flow meter/controller (LINDE FM 4575). A thermal electron $NO_x$ analyzer (Chemiluminescent $NO_x$ analyzer) was used for $NO_x$ analysis. The $NO_x$ analyzer was always on-line providing a continuous reading of parts per million (ppm) concentration being produced from the reaction chamber. The flow meter was in conjunction with a mass flow controller (Linde 10C 202 4124). The flow lines were stainless steel 1/4 inch T304 tubes.

## 2. 2 Experimental procedure

Compressed dry air was fed to the plasma reactor through a flow meter/controller in the range of 0 to 500 ml/min as a reactant. To maintain enough pressure for venting the gas after it went through the analyzer a small vacuum pump was connected downstream of the analyzer at the sample port.

The initial step was to establish a steady flow rate of the gases and to check the flow lines for leakage. The flow rate was set at 100 ml/min and the line pressure was set at 23 psig. The primary voltage was set at 90 V. The secondary voltage and power was high at 60 Hz because the rating of the transformer was set at this particular value for commercial applications. In the next step the frequency of the current to primary voltage was varied in increments of 10 Hz from 60 Hz to 650 Hz at each primary voltages. To account for residence time, the flow rate of the gas was increased in a certain increment. The effect of relative humidity was studied by bubbling the gas through a series of Erlenmeyer flasks.

## 3. RESULTS AND DISCUSSION

### 3. 1 Effect of frequency on power and secondary voltage

Fig. 2 shows power in an open circuit test for a transformer specially manufactured for this experiment. An open circuit in this case would imply no load on the transformer. Once the maximum has been linearly reached the power drawn remains constant, there was no more increase in the power with an increase in the frequency, which would mean the power drawn was remained constant. Fig. 3 shows secondary voltage variation in an open circuit test for a transformer used. The secondary voltage does not show the same characteristics as power. The increase in the secondary voltage is not linear, whereas exponential at high frequencies as shown in Fig. 3. These are characteristic curves for the

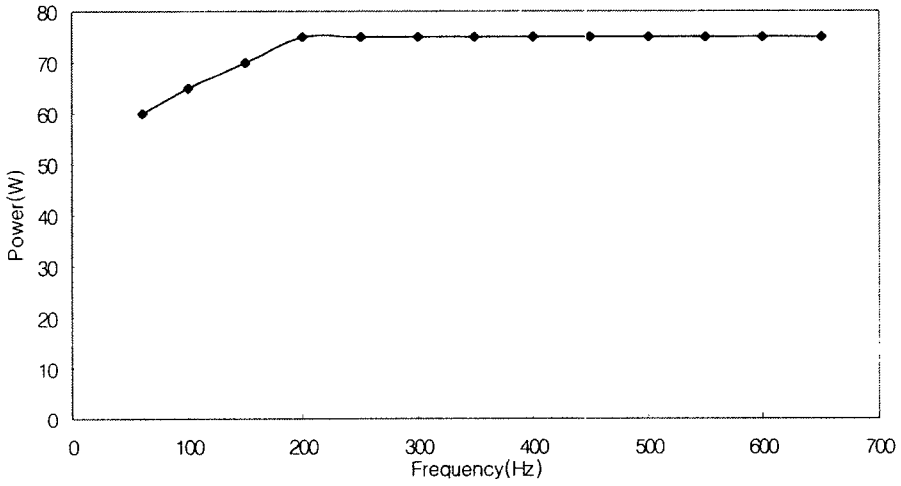


**Fig. 2. Effect of frequency on power in an open circuit for the transformer used at a fixed primary volt of 60.**

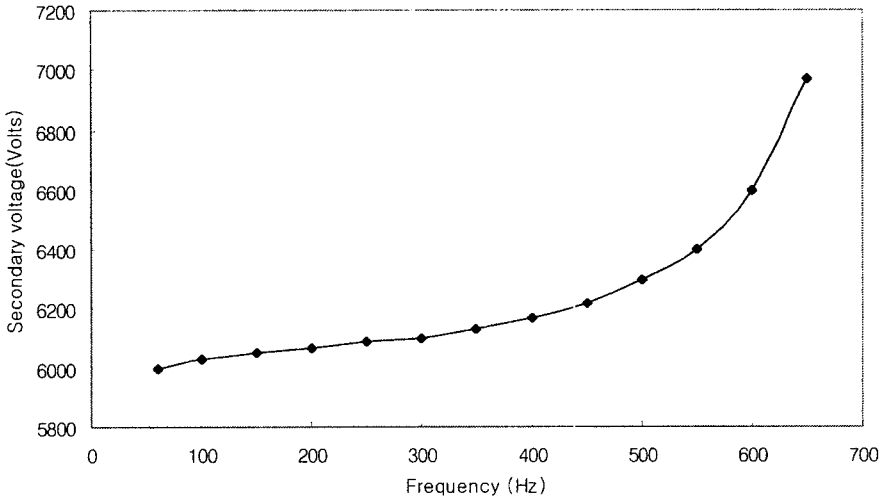


**Fig. 3. Effect of frequency on secondary voltage in an open circuit for the transformer used at a fixed primary volt of 60.**

transformer specially designed and made for this study. Each transformer has different characteristic curves so that it should be checked for the optimization of the system.

### 3. 2 Effect of primary voltage and frequency on power and secondary voltage

The breakdown of the gas is influenced by the characteristics of the transformer along with nature of the dielectric of the gas and the reactor material. Thus the ACPR needs to be tuned to attain a steady plasma and cause a break down of the gas. Tune point is the frequency at which the breakdown of the gas is initiated. However, for electronegative gases, which could produce a large amount of negative-ion space charges upon ionization, the breakdown characteristics (Loeb, 1939) were found to be very irregular.

Fig. 4 shows the effect of primary voltage on power under conditions of flow rate 200 ml/min and relative humidity (RH) 0%. It can be observed from Fig. 4 that as the frequency was increased at a fixed primary of 60 volts from 60 Hz to 650 Hz the power decreased slowly from 65 watts to 55 watts and then increased 85 watts at the frequency of about 500 Hz. Whereas, the power at a fixed primary of 90 volts decreased slowly from 80 watts to 65 watts as the frequency increased from 60

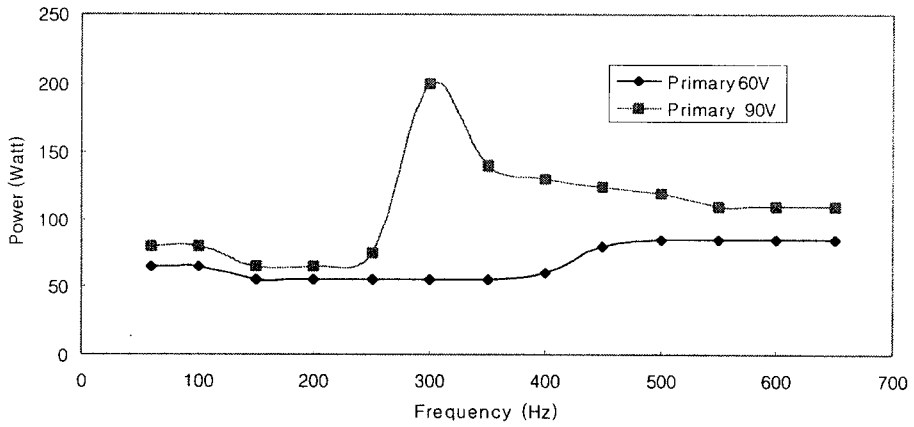


**Fig. 4. Effect of primary voltages on power with flow rate 200 ml/min, RH = 0%.**

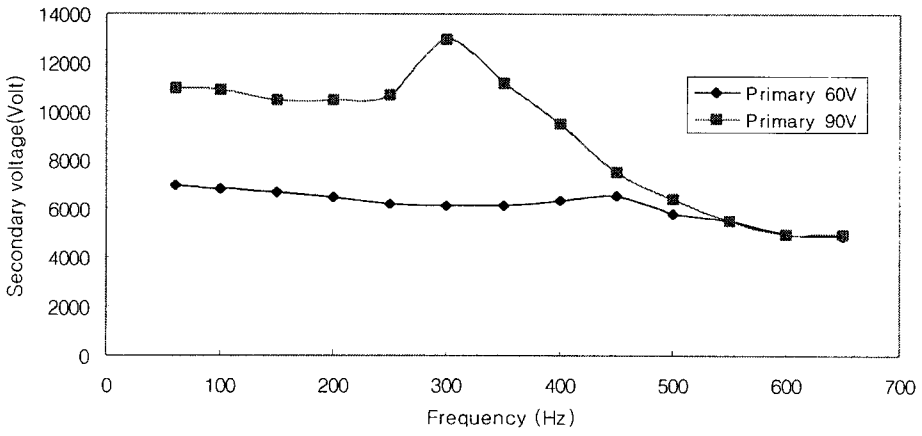


**Fig. 5. Effect of primary voltages on secondary voltage with frequency variation.**

Hz to 250 Hz and then increased sharply to 200 watts at the frequency of about 300 Hz. Further increases in the frequency caused a sharp drop of power to 140 watts at the frequency of about 350 Hz and then decreased slowly to 110 watts. At a certain frequency for a particular primary voltage, reactor power goes through a maximum and then begins to decrease with increasing frequency. The alternating current plasma reactor had an optimum frequency at each primary voltage which yielded a maximum power input to the reactor. Thus this peak is called the optimum condition. The optimum conditions were observed at certain values of frequencies for particular primary voltages as shown in Figs. 4 and 5. The reason for the optimum condition is believed to be a result of the secondary electrical circuit loading on the transformer. In Figs. 4 and 5 it can be also observed that the power and secondary voltage show the same behavior of sharp increase in the magnitude at breakdown. Once a breakdown was achieved by secondary voltage and power decreased rapidly with frequency.

### 3. 3 Effect of frequency on $NO_x$ production

The production of $NO_x$ was not maximum at the peak value of power and secondary voltage as shown in Figs. 6 and 7. In Fig. 6 observed was that at breakdown the frequency was about 300 Hz and the breakdown voltage was about 12,400 volts. The corresponding power was about 195 watts but the $NO_x$ concentration was only 255 ppm which was much below the maximum concentration. As frequency was increased the secondary voltage and the power decreased but the concentration increased rapidly. At a maximum concentration of about 745 ppm the frequency and secondary voltage was 600 Hz and 4,200 volts, respectively, and the power drawn from the wall was just 110 watts. It could be observed here that the frequency was an important parameter in the production of $NO_x$. The polarity change rate of electrodes increases as the frequency is increased. This increases the number of collisions an electron has with other ions and radicals. Increased collisions lead to formation of more nitrogen oxides. However high frequencies also decrease the magnitude of the secondary voltage. At low secondary voltages it was difficult to maintain the plasma. Once the plasma was lost, a sudden and sharp decrease in the formation of nitrogen oxides was observed.

Figs. 6 and 7 also show that the maximum $NO_x$ was produced at 918 and 745 ppm for the residence times of 27 and 13.5 sec, respectively. It can be inferred that as the flow rate increases the conversion of air to $NO_x$ decreases. In another word, the less energy imparted to the reactants, the less decomposition, and of course the less recombination of the by-products forming $NO_x$ will be.

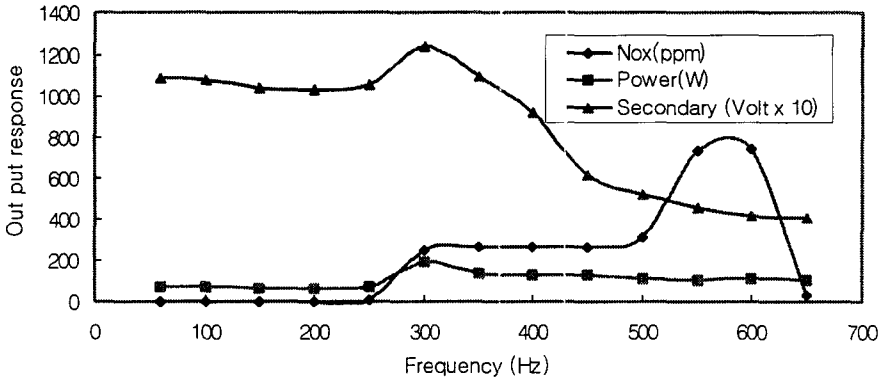


**Fig. 6. Effect of frequency on concentration of nitrogen oxides with residence time of 13.5 sec at flow rate 200 ml/min under relative humidity 0.0%.**

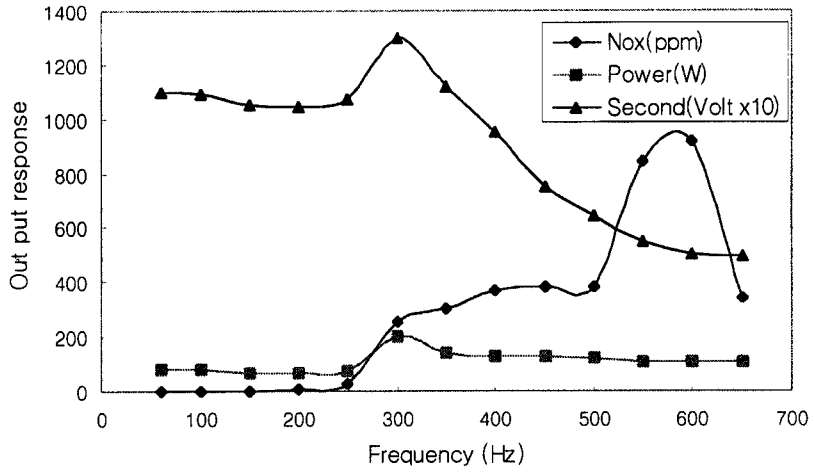


**Fig. 7. Effect of frequency on concentration of nitrogen oxides with residence time of 27 sec at flow rate 100 ml/min under relative humidity 0.0%.**

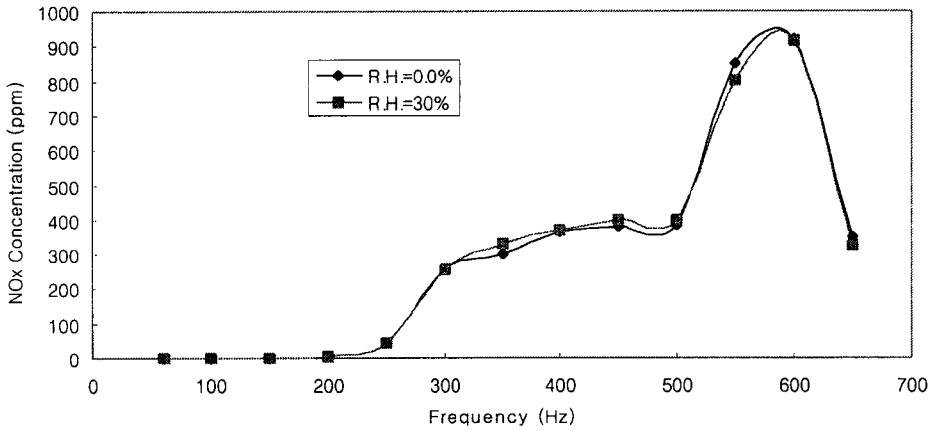


**Fig. 8. Effect of humidity on $NO_x$ production.**

### 3. 4 Effect of humidity on $NO_x$ productions

Fig. 9 shows the amount of $NO_x$ produced for the flow rate of 100 ml/min at the primary voltage of 90 volts. All tests were performed at the optimized 90 volts setting with a frequency of 300 Hz. The results of these experiments are presented in a graphical manner and are discussed as follows. As the air stream's moisture content was increased, $NO_x$ production increased to it's maximum of 1,810 ppm at 38% of relative humidity. As relative humidity was further increased, the enhanced $NO_x$ production rapidly dropped to the background level of 3 ppm in the breathing air. A possible explanation for this behavior stems from a combination of two things. First, the difference in bond energies of $N_2$ and water. And second, the reaction of the oxides of nitrogen formed in the plasma chamber was not detected by the $NO_x$ analyzer with radicals formed by the decomposition of water since the $NO_x$ analyzer ultimately only detects NO and $NO_2$. Various oxides of nitrogen may be formed in the reaction chamber, but when

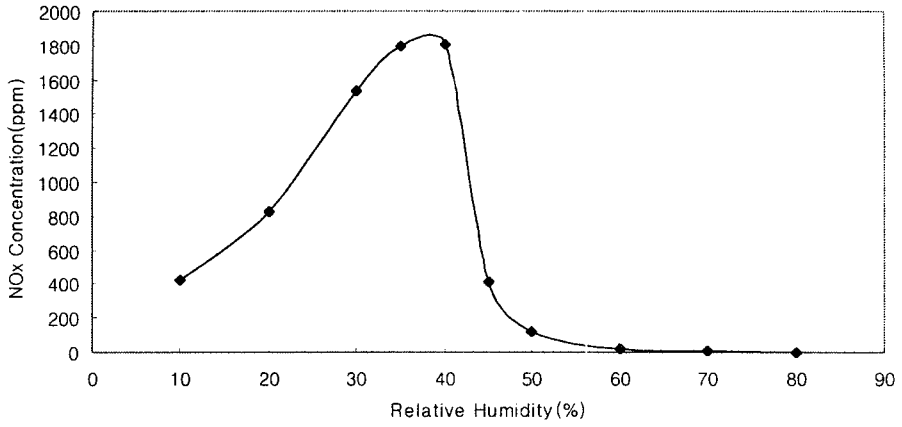


**Fig. 9. $NO_x$ production with respect to relative humidity at primary voltage 90 V and flow rate 100 ml/min.**

the sample enters the analyzer the gas passes through the conversion chamber. This exposure to extreme heat may convert some higher oxides to the more basic nitrogen oxides. For example, $N_2O_4$ may be broken down to $NO_2$ and $NO_2$. Qualtative analysis has never been done yet to determine all of the oxides of nitrogen produced by the ACPR. The following sections are hypothetical and require further investigation to prove or disprove. Based on inorganic chemical reactions that are known to occur naturally, the radicals resulting from the decomposition of water are H, OH, $H^+$ and $OH^-$. Moeller (1952) lists the following naturally occurring reactions involving various oxides of nitrogen:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The above reaction represents the equilibrium of $NH_3$ and $O_2$ with NO and $H_2O$ possibly existing in the plasma chamber. Ammonia is not a known product of the discharge chamber, but due to the existence of nitrogen and hydrogen with ample energy to drive chemical reactions, it is possible that ammonia could be formed in the reaction chamber. The increased $NO_x$ production could be explained by this reaction if ammonia produced in the discharge chamber was enhanced by the addition of humidity. The hydrogen radicals introduced by the decomposition of water vapor could react with the nitrogen radicals increasing the ammonia concentration past the equilibrium value. This would in turn, shift the equilibrium to the right, resulting in an increase in the $NO_x$ concentration indicated by the Analyzer.

Another possible mechanism for increased $NO_x$ production with the addition of humidity is:

$$N_2O_2^{-2} + 4OH^- \leftrightarrow 2NO_2^- + 2H_2O + 4e^-$$

If the production of $NO_2^-$ is enhanced by the addition of water vapor to the chamber, the equilibrium could shift to left resulting in an increase in $N_2O_2^{-2}$. High levels of $N_2O_2^{-2}$ in the chamber could possibly produce NC by the following reaction (Moeller, 1952):

$$N_2O_2^{-2} \leftrightarrow 2NO + 2e^-$$

In the above reaction, $N_2O_2^{-2}$ from the previous proposed mechanism may be present over the equilibrium concentration, shifting the reaction to produce more NO. The above reactions cited represent just a few of the possible mechanisms that could lead to the increased production of $NO_x$. Thus the sharp peak at 38% of relative humidity showed that the $NO_x$ production was not a one dimensional phenomenon.

Above 40% of relative humidity, the enhanced production was choked off and production rapidly dropped to 3 ppm since the corona energy is not enough to decompose an appreciable amount of $N_2$ after attacking

all water molecules. A possible explanation for this behavior stems from bond energy difference between $N_2$ and $H_2O$.

Nitrogen has a triple bond with an energy of 946 kJ, while water's bond energy is about 463 kJ. The water will absorb the corona power before the nitrogen since it requires less energy to break the bond, therefore it is more susceptible to decomposition. If water vapor is present, the electrons and radicals will attack water molecules rather that the oxygen molecules corona attacks the most vulnerable species in the reaction chamber (Coffman and Browne, 1965). The above explanation can be proved by the effect of the relative humidity concentration on $NO_x$ production as shown in Fig. 8. It was observed that there was no difference of the $NO_x$ productions in the range of the relative humidity 0 to 30%.

## 4. CONCLUSIONS

The alternating current plasma reactor had an optimum frequency at each primary voltage which yielded a maximum power input to the reactor. $NO_x$ production was increased as primary voltage increased and the flow rate decreased. Influence of humidity was the most notable with regard to the production of $NO_x$ in this research work. In another word, there was a maximum point for the production of nitrogen oxides which depended on the relative humidity. The above statement provides further insight into corona behavior. Assuming the corona attacks the most vulnerable molecules in the reaction chamber before attacking other more tightly bonded molecules, possibly at humidities above 38% and the optimized 90 volt setting, there is not enough energy left after attacking all water molecules to decompose an appreciable amount of $N_2$. If no nitrogen breakdown occurs, then no oxides of nitrogen will result. Of course, further research needs to be done linking molecule vulnerability and byproduct formation in the reactor.

The production conditions of $NO_x$ could be applied to prove in more detail the destruction mechanism of $NO_x$ by plasma and to use in the design for a concentric ACPR.

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