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Effect of Gas Composition on Ozone Generation in Silent Discharge Process

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Abstract

The effect of gas composition on the discharge characteristics and the ozone production in silent discharge (SD) process was investigated. The major gas components, N_2, O_2, and H_2O influence the discharge properties according to their relative magnitude of ionization thresholds and electron affinities. The generated amount of ozone increased with the discharge energy by increasing the electron mean energy. The higher oxygen content injected, the higher ozone produced. A small amount of water vapor significantly lowered the discharge onset voltage by the ionization threshold decreasing effect and high electrical conductivity. However, the further increase of water vapor contributes to decrease the electron density by the electron affinity. The addition of water greatly reduced the ozone generation through the formation of OH radical and the catalytic ozone destruction process.

Key words : Silent discharge (SD), Ozone generation, Discharge properties, Gas composition

1. INTRODUCTION

Ozone (O_3) has been widely used in many industrial and environmental application fields such as potable and waste water treatments, odor and air pollutant decomposition, chemical synthesis, pulp bleaching, measurement of material corrosion resistance, and others. The efficient and reliable O_3 generator is required for large-scale applications. Several types of commercial scale O_3 generators presently are available. The representative processes are silent discharges (SD), electrolysis, and ultraviolet irradiation (Carlins and Clark, 1982; DuRon, 1982; Foller, 1982). The most widely applied process is based on the silent discharge technology which was developed by Siemens in 1857 (Kogelschatz and Eliasson, 1995).

The first step towards O_3 formation in the SD is dissociation of oxygen molecules by electron impact. Starting from ground state oxygen molecules two paths of the reaction towards dissociation are available (reactions (1) and (2)). Then ozone is formed in a three-body reaction of O and O_2 leading to the O_3 molecules (reaction (3)).

$$e+O_2 \rightarrow e+O_2(A^3\Sigma_u^+) \rightarrow e+O(^3P)+O(^3P) \quad (1)$$
$$e+O_2 \rightarrow e+O_2(B^3\Sigma_u^-) \rightarrow e+O(^1D)+O(^3P) \quad (2)$$
$$O+O_2+M \rightarrow O_3^*+M \rightarrow O_3+M \quad (3)$$

The major O_3 application to the environmental fields is the conventional water treatment process. It is necessary to generate the high concentration ozone because the gas-liquid mass transfer is important for an efficient process operation. Therefore, the high yield of O_3 is pursued in commercial ozone generators by various

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supplementary equipments such as cooling system, dry system, pure oxygen producing unit, and so on (Carlins and Clark, 1982).

Recently, many types of electrical discharges have been used to destroy gaseous air pollutants such as volatile organic compounds (VOCs), odor, microorganisms, and others (Won *et al.*, 2001; Lee and Jung, 2000; Urashima and Chang, 2000; Chang and Chang, 1997). Electrical discharges contribute to generate various active chemical species as well as ozone, which participate in pollutant destruction. In these processes, the homogeneous gas phase reactions between low concentration pollutants and active species are very important. The optimum operating conditions are different according to physical and chemical properties of target pollutant to be removed. Therefore, it is necessary to find the optimum conditions fit to the special applications. One of important research objectives in these applications is the development of simple, cheap, reliable, and energy efficient discharge systems than that of high yield of specific chemical species. In this study, we investigated effects of gas composition on the O_3 generation to evaluate physical, electrical, and chemical properties of silent discharge process for air pollution control applications.

2. EXPERIMENTAL

Figure 1 shows the schematic diagram of the experimental set-up, which consists of gas injection parts, a power supply unit, and a silent discharge (SD) reactor.

The gas streams were controlled using flow meters (KOFLOC). The inlet gas composition was adjusted by controlling the mixing ratio of pure N_2 and O_2. The humidity control of air streams was done by passing air through the water sustained in controlled temperature. The rod to cylinder type SD reactor was used to generate ozone in the experiment. The reactor was made of a glass tube with the inner diameter of 20 mm, the thickness of 2 mm, and the length of 500 mm. The inner electrode was made of a copper rod with the diameter of 16 mm. The gap distance passing the gas streams was 2 mm. A copper film tape was wrapped around the glass tube and served as the outer electrode. The length and volume of the electrically active zone were 300 mm and 33.93 cm^3.

The AC high voltage was applied to the SD reactor. A 15000× transformer (Daehan, 160VA) and a voltage adjuster (Busan electronics, 2 kVA) were used to produce the high alternating voltages with the frequency

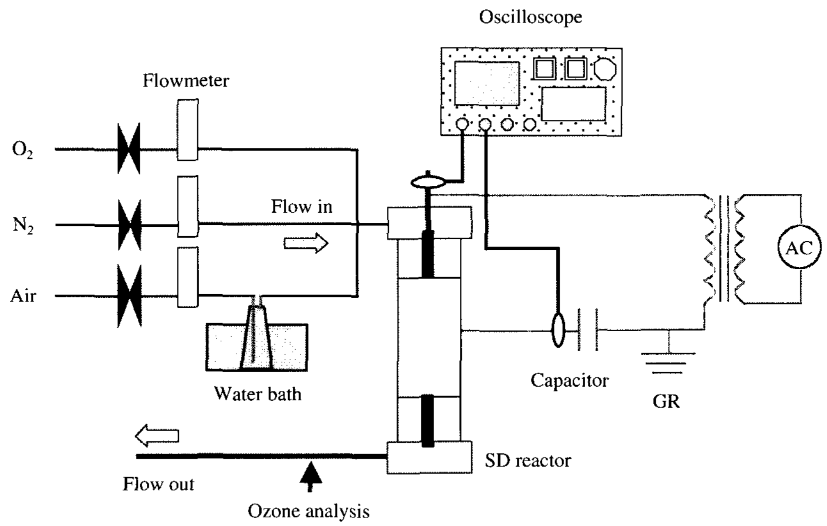

Fig. 1. Schematic diagram of experimental set-up.

Table 1. Typical operating parameters and ranges.

	Parameters	Operating ranges
Fixed reactor parameters	Inner diameter of reactor (mm)	20
	Length of outer electrode (mm)	300
	Dielectric thickness (mm)	2
	Inner electrode diameter (mm)	16
Electrical parameters	Voltage (kV peak)	0~20
	Frequency (Hz)	60
	Energy (mJ/cycle)	0~320
Operating parameters	Gas retention time (sec)	1, 2
	O_2 content in N_2 (%)	0, 5, 10, 15, 20, 30, 50, 100
	Humidity in air (%)	0, 2.35, 4.37

of 60 Hz. Electrical parameters were controlled at the voltage control mode. Typical experimental conditions are summarized in Table 1.

The oscilloscope (Lecroy, LT354) was used to measure electrical properties of the system. A 1000× high voltage probe (Lecroy, PPE20KV) was used to measure high voltages applied to the reactor. A capacitor (1 μF) was connected to the reactor in series to measure the discharge current and the charge. A 100× divider (Lecroy, PPE5KV) was used to measure the voltage across the capacitor. The ozone concentration was analyzed by KI method. The outlet gas streams were passed through the 2% potassium iodide solution and titrated with sodium thiosulfate. All experiments were carried out at ambient temperature and pressure.

3. RESULTS AND DISCUSSION

3. 1 Oxygen content effect

Figure 2 shows discharge onset voltages (V_{ON}) with the oxygen content. Gas discharges started with the application of 9 kV and 7 kV in pure N_2 and O_2 streams, respectively. When the mixture of O_2 and N_2 was injected to the reactor, the discharge onset value was 8 kV irrespective of the composition. We can understand these results by the comparison of the ionization thresholds of O_2 and N_2. The ionization thresholds of O_2 and N_2 are 12.2 eV and 15.6 eV, respectively. The addition of oxygen having the lower ionization energy

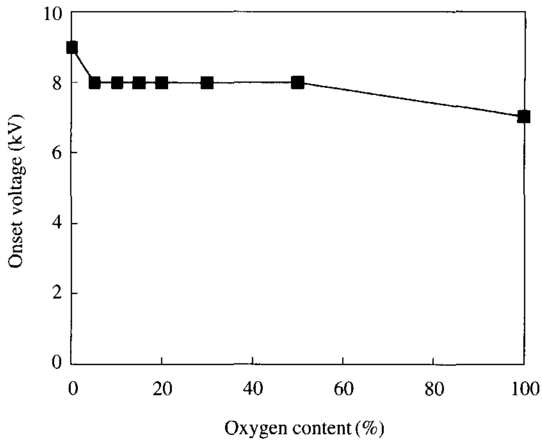

Fig. 2. Effect of oxygen content on discharge onset voltage.

increases the degree of ionization of gas streams and therefore, decreases the discharge onset voltage.

The discharge energy (E_{DIS}) transferred to gas streams during a cycle of AC voltage can be calculated from integrating the product of voltage and current values with a period of waveforms. Figure 3 shows the effect of oxygen content on the discharge energy according to the applied voltage. One may see that the discharge energy increases with the applied voltage in all gas composition. The oxygen content effect on the discharge energy shows two trends according to the range of O_2 content. In the low oxygen content region up to approximately 10%, the discharge energy increased with the O_2 content. When the O_2 content was higher than 10%, however the distinct effect was not observed.

The oxygen in N_2 streams can affect gas discharges in two ways. The O_2 doest not have only a low ionization threshold as described above, but also has high electro-negative nature (electron affinity) than N_2 molecules. The addition of a small amount of O_2 can enhance the gas discharges because it lowers the ionization potential of gas streams. However, the oxygen addition over a certain limit can participate in deteriorating the discharges as well as enhancing the discharges. Therefore the obvious oxygen effect is not

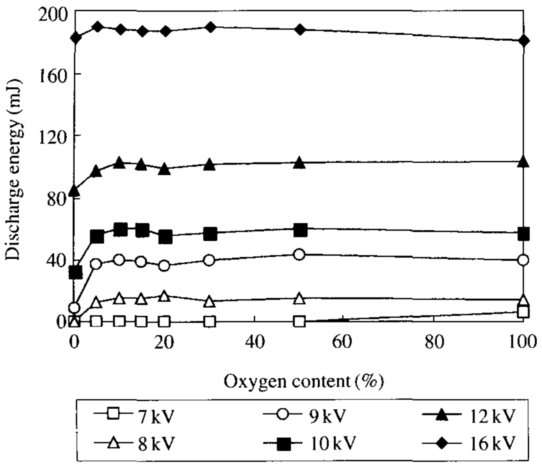

Fig. 3. Effect of oxygen content and applied voltage on discharge energy.

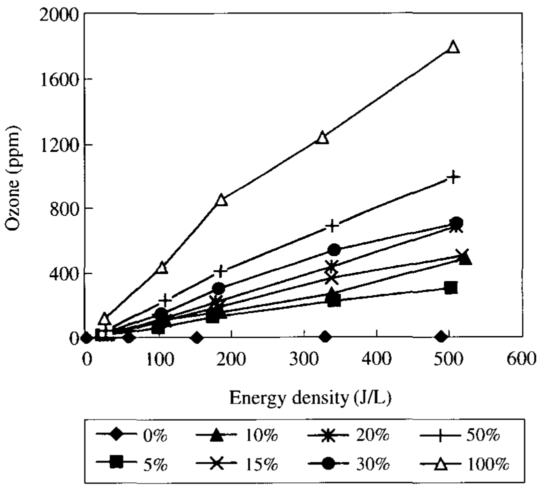

Fig. 4. Ozone generation with energy density as a function of oxygen content.

observed in O_2 content ranges over the limit.

The effect of the O_2 content on the ozone generation with the discharge energy is shown in Fig. 4. The energy value of abscissa is the energy density, which means the discharge energy transferred to the unit flow rate of gas streams. The O_3 generation almost linearly increased with the energy in all O_2 contents except 0%. And also, the increase of the O_3 was observed with the

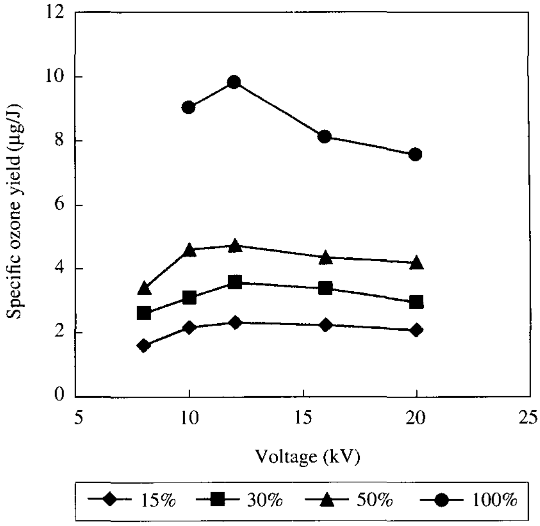

Fig. 5. Effect of voltage and oxygen content on specific ozone yield.

O_2 content at the same energy condition. The results can be understood by the consideration of the O_3 generation mechanisms shown in reactions from (1) to (3).

The initial step of the O_3 generation is the dissociation of O_2 molecules by electron impact. The electrons having an average energy of about 6~9 eV effectively participate in the dissociation of oxygen molecules (Kogelschatz, 2000). The increase of the applied voltage increases the discharge energy and the mean electron energy. Therefore the higher voltage is applied to the reactor, the more oxygen atoms taking part in O_3 generation are produced. The enhancement of the O_3 generation with oxygen content is caused by the increment of oxygen atoms because the oxygen molecules are the source of O atoms.

The energy efficiency of the O_3 generation can be indicated by the specific ozone yield, which is defined as the ratio of produced O_3 mass to the unit electrical energy transfer. Figure 5 shows effects of the applied voltage and the O_2 content on the specific O_3 yield. One may see that the O_3 yield increases with the O_2 content. The results also show the presence of a certain voltage, which is able to obtain the maximum O_3 yield.

The plasma in gas discharges consists of various charge carriers such as O^+, O_2^+, O^-, O_2^-, O_3^-, N^+, N_2^+, and excited atomic and molecular species as well as free electrons. Since ionic reactions do not noticeably contribute to the O_3 formation, energy losses due to ionic species lowers the energy efficiency of the O_3 generation. Calculations and experiments show that a considerable fraction of the discharge energy (up to 50%) can be dissipated by ionic species in weak discharges (Kogelschatz, 2000). The situation improves when, at higher electron and ion densities, recombination becomes faster than the time for ions to drift through the gap. In the limiting case of high electron densities, the most energy is practically dissipated by electrons while the ions are more or less stationary during the discharges (Eliasson *et al.*, 1987). However, when the discharges become too strong by the voltage application over a certain limit, the O_3 generation is deteriorated by undesired chemical side reactions (Nilsson and Eninger, 1997). We can see that the optimum voltage for the maximum O_3 yield is around 12 kV in the experimental conditions.

3. 2 Humidity effect

The effect of the humidity on discharge onset voltage and energy is shown in Fig. 6. The gas discharges started with the voltage of 8 kV. When 2.35% and 4.37 % of water vapor were added to air streams, the onset values were significantly decreased to 4 kV and 5 kV, respectively. One may also see that the discharge energy increases with the humidity in the lower voltages up to 10 kV. However the increment of the discharge energy goes to small amounts as increasing the voltage. The H_2O addition decreases the ionization threshold of air streams because the H_2O has the lower ionization threshold (13.7 eV) than N_2 molecules and the higher electrical conductivity than other gas components. In addition to these properties, the H_2O also has higher electron affinity, so it can contribute to decrease the electron density. The results in the figure show that a small amount of H_2O significantly lowers the discharge onset voltage and increases the discharge energy by the ionization threshold decreasing effect and high electrical conductivity. However, the further increase of H_2O contributes to decrease the electron density by the electron affinity nature.

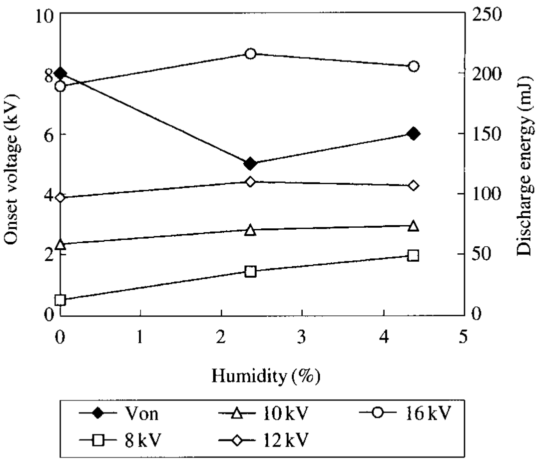

Fig. 6. Effect of humidity on discharge onset voltage and energy.

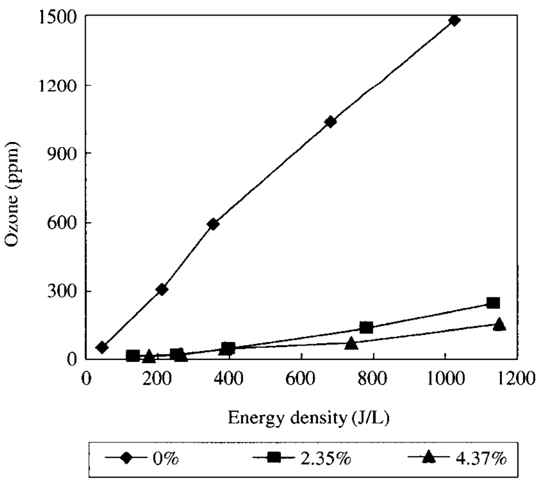

Fig. 7. Effect of humidity on ozone generation.

Figure 7 shows the effect of humidity on the O_3 generation. It is observed that the O_3 generation was significantly deteriorated by the H_2O addition. Ozone formation reactions in the presence of H_2O vapor are influenced by the generation of OH radicals. The OH

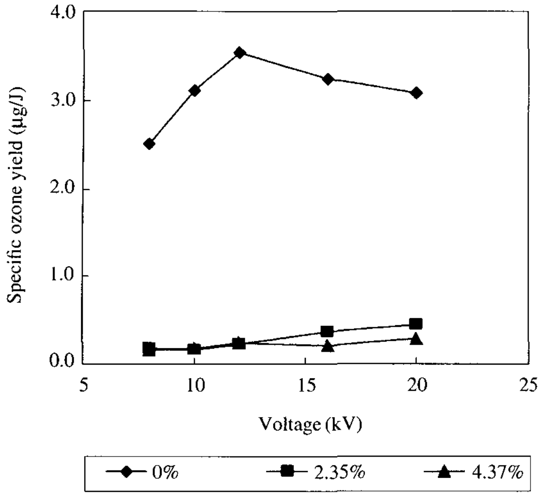

Fig. 8. Effect of humidity and applied voltage on specific ozone yield.

radicals can be formed by electron impact dissociation of H_2O and, in most cases more importantly, by fast reactions of electronically excited O atoms and N_2 molecules (Kogelschatz, 2000). OH radicals decompose ozone molecules by catalytic O_3 destruction process. The following chemical reactions show the OH radical formation in discharges and the O_3 destruction mechanisms.

$$e+H_2O \rightarrow OH+H \quad (4)$$
$$O(^1D)+H_2O \rightarrow 2OH \quad (5)$$
$$N_2(A^3\Sigma_u^+)+H_2O \rightarrow N_2+OH+H \quad (6)$$
$$OH+O_3 \rightarrow HO_2+O_2 \quad (7)$$
$$HO_2+O_3 \rightarrow OH+2O_2 \quad (8)$$

Effects of the applied voltage and the H_2O content on the specific ozone yield are shown in Fig. 8. The specific O_3 yield is reduced to several tens times decreased values by the humidity. We can also observe the optimum voltage value for the maximum ozone yield is present in dry air streams but there is not the optimum voltage in the case of wet air streams. This phenomena was not obviously understood, however it seems to be caused by the fact that O_3 destruction process is very fast in the wet air streams. The electron formation increases at the higher voltage condition though other ionic species also increase. Therefore the O_3 yield can be increased with the voltage in wet air streams.

4. CONCLUSIONS

The effect of gas composition on the O_3 production in silent discharge (SD) process was investigated. The electrical properties such as discharge onset voltage (V_{ON}) and energy (E_{DIS}) were influenced by the gas composition and humidity. The major gas components, N_2, O_2, and H_2O affect the discharge characteristics according to their relative magnitude of ionization thresholds and electron affinities. Because the O_2 in N_2 streams lowers the ionization threshold, the discharge onset voltage was decreased by the O_2 addition. The discharge energy increased with the O_2 addition up to approximately 10% by the ionization threshold decreasing effect. However, further O_2 addition has not distinct effect on the discharge energy by the offset between ionization threshold decreasing and electron affinity increasing effects. The increase of the discharge energy enhanced the O_3 generation by increasing the electron mean energy. The O_3 generation increased with the O_2 content which was the source of O atoms participating O_3 synthesis. The discharge onset voltage was lowered by small amount of H_2O and the discharge energy increased with the humidity at low voltage application by the ionization threshold decreasing effect and the high electrical conductivity. But the further increase of H_2O contributed to decrease the electron density by the electron affinity. The H_2O addition significantly reduced the ozone generation through the OH radical formation and the catalytic O_3 destruction process.

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