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Oxidation of Volatile Organic Compounds by Using a Microwave-Induced Plasma Process

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Abstract–A microwave plasma system using a 2.45 GHz magnetron was applied to the decomposition of volatile organic compounds such as toluene and trichloroethylene. Designed for producing plasma at atmospheric pressure, this microwave plasma system consists of a magnetron detached from a household microwave oven, a directional coupler, a three-stub tuner, a tapered waveguide, and plasma flame section where a quartz tube with a nozzle is located. In this system, the organic compounds can be decomposed by thermal incineration as well as by reactions with various active species formed during plasma discharge. The effect of feed gas flow rate on the decomposition was significant due to the decrease in the gas temperature, but the initial concentration in the range of 210-2,100 ppm did not largely affect the decomposition efficiency. The principal byproduct was nitrogen oxides because this system was operated at high temperature. To improve the decomposition of the organic compounds, argon was used as a plasma-assisting gas, together with the air-like feed gas mixture. Large enhancement in the decomposition efficiency was achieved by the use of argon.

Key words: Microwave, Plasma, Volatile Organic Compounds, Decomposition

INTRODUCTION

Volatile organic compounds (VOCs) emitted from many sources including chemical manufacturing plants, semiconductor industry and paint industry cause various environmental problems such as photochemical smog, greenhouse effect, stratospheric ozone depletion, and carcinogenic effects. Conventional methods available for VOCs treatment are adsorption, catalytic oxidation and thermal oxidation [Yan et al., 1998; Cooper and Alley, 1994; Cho et al., 1999; Kim and Lee, 2001; Song et al., 2002; Kim et al., 2002], and recently many studies on non-thermal plasma processes such as dielectric barrier discharge and pulsed corona discharge have been reported to be effective for the decomposition of VOCs [Oda et al., 1996; Kohno et al., 1998; Futamura et al., 1999; Choi et al., 2000; Jeong et al., 2001; Moon and Chae, 2001]. However, incomplete oxidation of organic compounds is typical of non-thermal plasma [Snyder and Anderson, 1998], i.e., carbon monoxide and various organic fragments with lower molecular weights including methane, propylene and formaldehyde are produced as byproducts. Moreover, ozone formation in the plasma reactor has also been pointed out as a significant problem [Moon and Chae, 2001].

One of the other methods producing plasma at atmospheric pressure is to use microwaves. An intense microwave field in waveguide accelerates electrons to give energetic ones that can ionize gas molecules, leading to the plasma state [Uhm, 1998]. Microwave plasma discharge can readily produce large amounts of a variety of active species such as radicals, ions and excited molecules. As a result, this process can induce effective chemical reactions [Baeva et al., 2001]. At present, the study on the application of microwave plasma discharge to the chemical reactions is in rudimentary stage, and only few studies have been performed for the reforming of natural gas, the removal of nitric oxide and the decomposition of perfluorocarbons (PFCs) produced in the semiconductor industry [Bailin et al., 1975; Baeva et al., 2001; Cho et al., 1998a, b; Wojtowicz et al., 2001; von Hagen et al., 2001].

The treatment of VOCs using microwave plasma discharge may mitigate the problem related to the production of harmful byproducts of low molecular weights such as formaldehyde and carbon monoxide because the gas temperature can be increased high enough to oxidize VOCs completely. Therefore, the difficulties with conventional non-thermal plasma processes can be settled without installing an oxidation catalytic reactor downstream the plasma reactor. In addition, ozone generation can essentially be repressed because the process is operated at high temperature. The magnetron, which is the microwave source, is the main part of the microwave plasma process. It is easily available since it is mass-produced for household microwave ovens. Such easy availability of the magnetron can be a merit of this process from the practical application and economic viewpoints.

There may be several points at issue for further improvement of the microwave plasma process. For practical use, this process should be able to produce plasma at atmospheric pressure. In vacuum, the mean free path of electrons is so long that generation and sustenance of plasma may be easy. On the contrary, at atmospheric pressure, generation and sustenance of plasma is relatively difficult, which should be solved for easy use of this process. As well, selection and optimization of design parameters is necessary to maximize

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‡This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

the conversion efficiency of electric energy into the generation of microwave plasma, resulting in the reduction of power consumption. Besides, it is necessary to generally examine the effects of several key variables on the decomposition of organic compounds and the formation of byproducts.

The present study reports a method for producing and keeping the plasma at atmospheric pressure and some primitive results for the decomposition of organic compounds. The organic compounds chosen in this study were toluene and trichloroethylene. The present microwave plasma system was designed in order that plasma may be produced and sustained at atmospheric pressure. The performance of this process for the decomposition of organic compounds was assessed with the variables such as feed gas flow rate and initial concentration. The major byproducts anticipated in this process are CO_2, CO and HCHO; and formation of nitrogen oxides is also expected because the microwave energy is used to heat the feed gas stream. These byproducts were also analyzed. In air-like gas mixture, vibrational excitation and dissociation of N_2 molecules may consume a large amount of electron energy [Kucukarpaci, 1979], resulting in lower decomposition efficiency of organic compound. To prevent such losses of electron energy, the possibility of using argon as a plasma-assisting gas was examined.

EXPERIMENTAL

Fig. 1 shows the schematic diagram of the experimental apparatus. A 2.45 GHz magnetron detached from a household microwave oven (Model OM75S, Samsung Electronics, Korea) was used as the microwave source for the production of plasma. The magnetron used generates, on average, 850±50 W RF power. Microwaves are transferred to the plasma reactor through the waveguide (W430). A 3-stub tuner and a sliding short were installed to minimize the reflected power by tuning them properly. A quartz tube of 38 mm in diameter that passes through the upper surface of the wide waveguide is the plasma reactor. A 2/5" commercially available copper nozzle of the oxygen-fuel torch cutter was vertically inserted from the bottom wall of the wide waveguide. This nozzle has a center hole and several side holes. The feed gas was injected into both the center hole and the side holes of this nozzle. The quartz tube can help one take out the treated gas for analyses although it is not necessary to produce plasma. The plasma was initiated by generating a spark between the grounded nozzle tip and the needle igniter operated with AC high voltage (16.5 kV). Once the plasma was ignited, it was able to be stably sustained even when the igniter was turned off. Although the temperature of the plasma produced was high, the nozzle did not melt since it was continuously cooled by the gas fed through it. The region around the quartz reactor was surrounded by a stainless steel net for electromagnetic shielding.

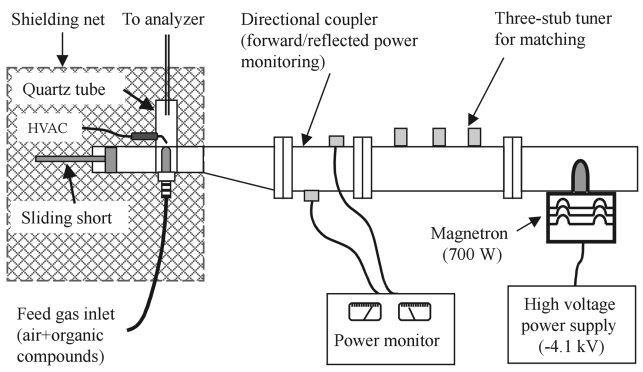

Fig. 1. Schematic of the 2.45 GHz microwave-induced plasma torch system.

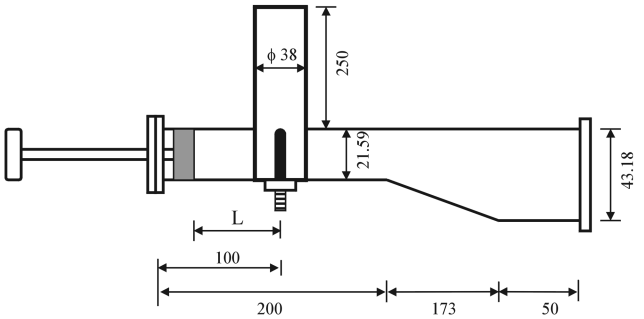

Fig. 2. Detailed diagram of the tapered waveguide equipped with the plasma reactor.

Since the electric field around the nozzle should be high enough to produce plasma effectively, the waveguide was tapered to half in height, i.e., the height of the waveguide was reduced from 43.18 mm to 21.59 mm with the width kept constant (86.36 mm). The detailed feature of the tapered waveguide is shown in Fig. 2. The optimal tapered length is related to the guide wavelength expressed as below [Park, 1991]:

$$\lambda_g = \frac{\lambda}{\sqrt{1-(\lambda/2a)^2}} \quad (1)$$

where λ_g is the guide wavelength, λ is the free space wavelength and a is the width of the waveguide. According to the simulation using HFSS computer code, the tapered length should be equal to the guide wavelength to minimize the return loss [Bae et al., 2002]. In case of 2.45 GHz, the free space wavelength is calculated to be 12.24 cm by a simple equation ($c=f\lambda$, c: speed of light; f: frequency; λ: wavelength). Using this value, the guide wavelength λ_g was found to be 17.3 cm.

The magnetron included in a household microwave oven generally uses half-wave voltage doubling circuit, as depicted in Fig. 3. Since the frequency of AC input is 60 Hz in the present case, the circuit gives 60 Hz high voltage pulse. Fig. 4 shows the waveform of the voltage applied to the cathode of the magnetron. The voltage is almost square wave with the pulse width of 8.3 ms, and its peak

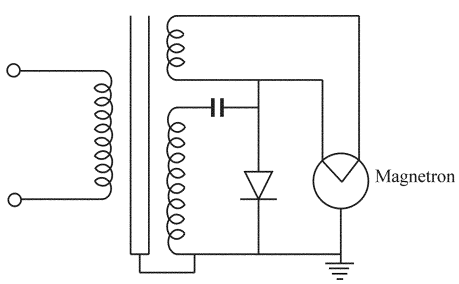

Fig. 3. Half-wave voltage doubling circuit for 2.45 GHz magnetron.

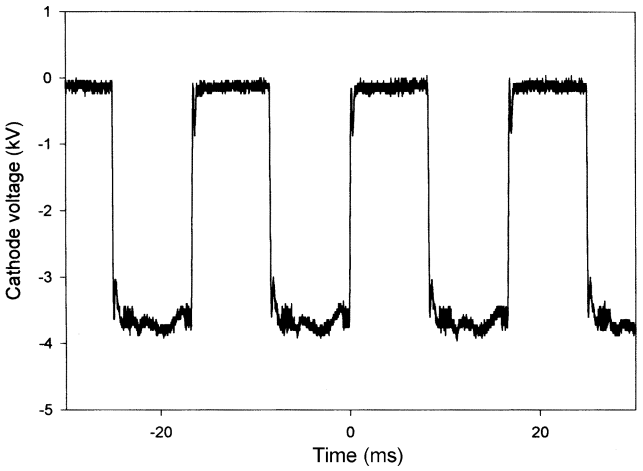

Fig. 4. Waveform of the cathode voltage applied to the magnetron.

value is about −4 kV. In principle, this kind of pulse voltage makes the RF power intermittent, and installing an igniter is necessary to initiate the production of plasma.

One of the volatile organic compounds chosen in this study was toluene, which is of the greatest importance in terms of the amount of emission. Toluene is classified as an aromatic compound, and it has been reported that the decomposition of toluene by using non-thermal plasma is very difficult due to its stability attributed to resonance hybrid and requires a large amount of energy [Mok et al., 2002]. If the microwave plasma process can successfully treat such chemically stable compounds, the other organic compounds are expected to be readily treated by this process. That is why toluene was chosen as the target compound in this study. The major component of the feed gas stream was air (N_2: 80% (v/v); O_2: 20% (v/v)). The concentration of toluene was adjusted by using its vapor pressure. A mass flask containing toluene was immersed in a refrigerating circulator kept at a constant temperature of 20 °C. At this temperature, the vapor pressure of toluene is 2.59 kPa. Nitrogen whose flow rate was regulated by a mass flow controller (Model 1179, MKS Instruments, Inc.) was saturated with toluene as it passed through the flask. When nitrogen is saturated at this temperature, the concentration of toluene corresponds to 25,570 ppm (parts per million, volumetric). This toluene-saturated nitrogen was later mixed with air, thereby diluted to a desired concentration. The concentration of toluene was changed from 210 to 2,100 ppm. The other organic compound chosen in this study was trichloroethylene, and its concentration was controlled to 1,000 ppm by the same method with that adopted for toluene. The flow rate of the feed gas stream was typically 10 L/min, and it was varied in the range of 5 to 15 L/min. So as to examine the effect of plasma-assisting gas on the decomposition of organic compounds, argon was used together with the air-like feed gas. The flow rates of argon and the feed gas were regulated by flow meters.

The net microwave power used for the production of plasma is the forward power minus the reflected power. The forward and reflected powers were measured by a directional coupler and a power monitor (MSTA Co., Korea). The AC input power was also measured by a digital power meter (WT200, Yokogawa, Japan). For the analysis of the organic compounds, a gas chromatograph equipped with a flame ionization detector (GC-14B, Shimadzu, Japan) was used. The decomposition efficiency of the organic compounds was found by measuring the difference in concentrations before and after plasma discharge. The byproducts such as CO and CO_2 were analyzed by flue gas analyzer (GreenLine, Eurotron, USA) and CO_2 monitor (Model 8762, TSI, Inc., USA), respectively, and for the measurement of formaldehyde, a chemical detector (Product number 91L, Gastec Co., Japan) was used. The concentration of NO_x formed in the reactor was analyzed by a chemiluminescence NO-NO_2-NO_x analyzer (Model 42C, Thermo Environmental Instruments, Inc., USA).

RESULTS AND DISCUSSION

The AC input power delivered to the magnetron system was measured to be 1.05 kW by a digital power meter. About 200 W was dissipated in the microwave generation circuit including cathode filament and high voltage transformer, and 850±50 W was converted into RF power. Fig. 5 shows an example of the forward and reflected power when the offset of the short (distance from the center of the nozzle to the sliding short) was 22 mm. The offset of

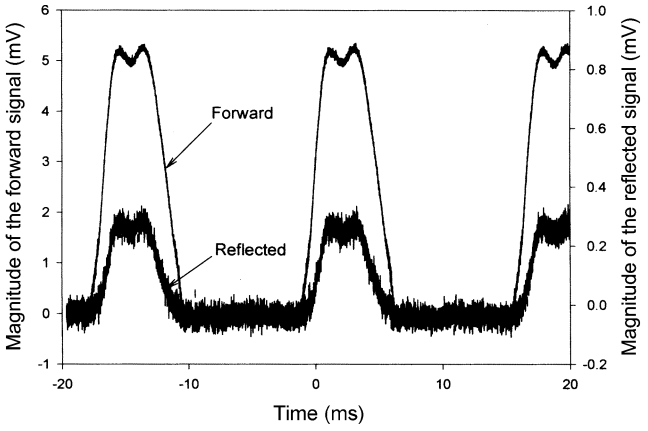

Fig. 5. Signals of the forward and reflected power converted into voltage.

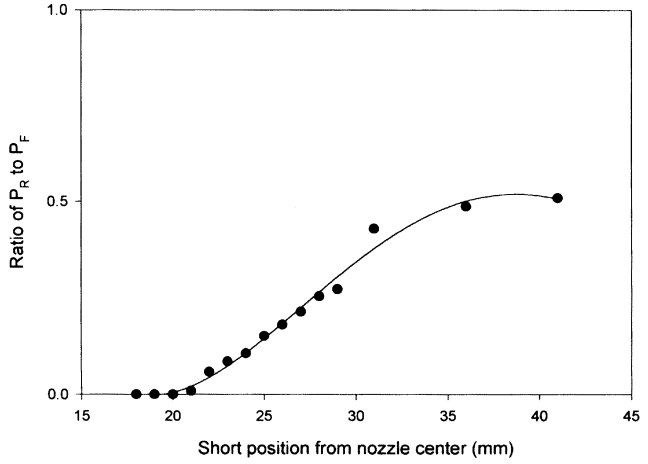

Fig. 6. Ratio of the reflected power to the forward power as a function of short position from the nozzle center (nozzle diameter: 10.2 mm; no air flow).

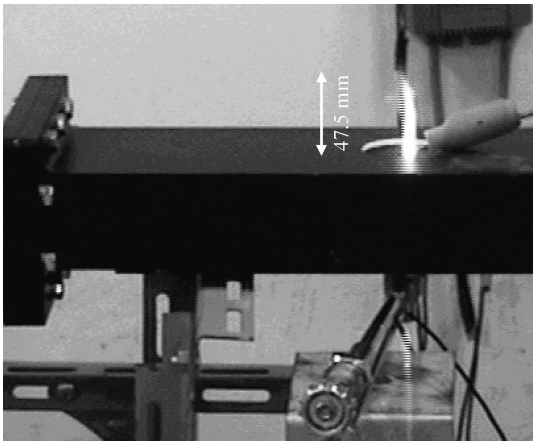

Fig. 7. Photograph of plasma flame (air flow rate: 10.0 L/min).

the short is expressed as L in Fig. 2. In this case, about 6% of the forward power was reflected, and thus 94% was used for the production of plasma. The reflected power can be minimized by adjusting the position of the sliding short. The ratio of the reflected power (P_R) to the forward power (P_F) as a function of the offset of the short is shown in Fig. 6. When the offset of the short was longer than 30 mm, the reflection ratio came to about 50%. However, the reflection ratio was minimized as the distance from the nozzle center to the short decreased to around 20 mm. Further experiments were carried out at this offset position of the short.

Fig. 7 presents a photograph of the microwave plasma discharge when the feed gas flow rate was 10 L/min. The plasma was initiated by generating a spark between the nozzle tip and the needle igniter. The plasma flame started from the nozzle tip and propagated upwards. Once the plasma was ignited, it was able to be stably sustained even when the igniter was turned off. Due to the high collision rate with surrounding gas molecules, the plasma flame appeared to be the same as the flame of the oxygen-fuel torch. The length and width of the plasma flame are related to the RF power dissipated for the production of plasma. In this experimental condition, the plasma flame was extended up to 4.7 cm at 20 mm offset of the short. As can be seen, the width of the plasma flame was very narrow, implying that the feed gas flow should be concentrated into the flame center for efficient treatment.

In case of non-thermal plasma processes, the principal reactions for toluene decomposition are known to be the charge transfer reactions of toluene with ions including N_2^+, O_2^+, N^+ and O^+ [Kohno et al., 1998; Sieck et al., 2001]. The charge transfer reactions and the relevant rate constants are summarized in the literature [Sieck et al., 2001]. As well, the energetic electron impact dissociations may provide additional decomposition channels [Kohno et al., 1998]. Besides such charge transfer reactions and energetic electron impact dissociations, thermal decomposition is believed to play an important role in the microwave plasma process because of high gas temperature. The effect of feed gas flow rate on the decomposition efficiency is depicted in Fig. 8. The decomposition efficiency was much lowered when the flow rate increased. The decrease in the decomposition efficiency with the increase in the flow rate may partly be explained by the decreased gas temperature. The adiabatic temperature increase can be calculated by using a simple equation

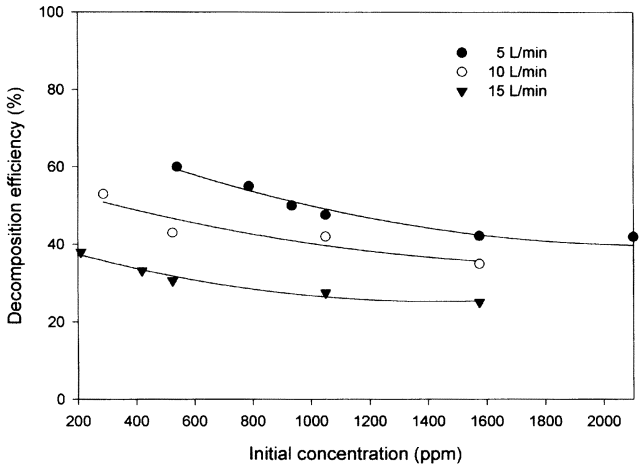

Fig. 8. Effect of the feed gas flow rate on the decomposition efficiency.

as follows:

$$q = \dot{m}\int_{T_1}^{T_2} c_p dT,\ c_p = \alpha + \beta T + \gamma T^{-2}\ (\text{cal/mol K}) \qquad (2)$$

Here, T_1 is the temperature of the feed gas entering the nozzle, i.e., 25 °C, and T_2 is the final temperature. In Eq. (2), $\dot{m}$ is the molar flow rate of the feed gas and equal to the product of the molar gas density (4.09×10^{-2} mol/L at 25 °C) and the volumetric flow rate. In case of air, the values of α, β and γ are 6.90, 9.2×10^{-4} and -1.76×10^{4}, respectively. To find T_2 by using this equation, energy delivery rate (power) should be known. In the absence of feed gas flow, the reflection ratio was reduced to 0.03 at the offset position of 20 mm (see Fig. 6). When the feed gas was injected to the nozzle, however, the reflection ratio increased. As observed in Fig. 9, the reflection ratio was about 0.2 at flow rates in the range of 5 to 15 L/min. Although it was not largely dependent on the flow rate, the reflection ratio in the presence of gas flow was relatively higher, compared to that in its absence. Taking this reflection loss into account, the net microwave power used for the production of plasma is 700 W (167 cal/s). With this energy delivery rate (power), Eq.

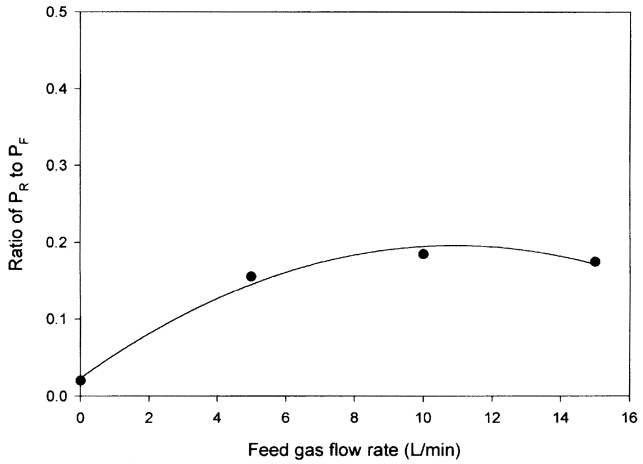

Fig. 9. Ratio of the reflected power to the forward power as a function of feed gas flow rate (offset of the short: 20 mm).

(2) can be solved in terms of T_2. When the gas flow rate at 25 °C was 10 L/min (0.167 L/s), T_2 was found to be 2,900 °C. The respective adiabatic temperatures at 5 and 15 L/min were calculated to be 5,170 and 2,050 °C. Since the reactor system was not isolated from natural cooling, the real gas temperature would be much lower than the adiabatic temperature. But, it is obvious that the increase in the flow rate caused the decrease in the decomposition efficiency. In addition, the decrease in the decomposition efficiency with the increase in the flow rate can also be explained with the decreases in relative amounts of active species such as N_2^+, O_2^+, N^+ and O^+ available for the decomposition. The number of active species is a function of power dissipated for the production of plasma. Thus, the concentration of the active species decreases with the increase in the flow rate when the power is identical.

One general trend appearing in Fig. 8 is that the decomposition efficiency did not largely depend on the initial concentration. For example, when the initial concentration was 250 ppm, about 55% of toluene was removed at a flow rate of 10 L/min. When the initial value was increased to 1,600 ppm at the same flow rate, the decomposition efficiency was about 40%. This decomposition efficiency is rather high, compared to the high initial concentration. In thermal incineration, the rate of decomposition is well described by a first order reaction [Cooper and Alley, 1994]. First order reaction means that the decomposition efficiency or the ratio of final to initial concentration is not a function of initial concentration. The weak dependency of the decomposition efficiency on the initial concentration implies that the thermal reaction plays an important part in the decomposition of toluene.

Fig. 10 presents the evolution of byproducts in the plasma reactor. Referring to the previous results, common non-thermal plasma processes using high voltage do not completely decompose VOCs into CO_2, and generate CO and various organic fragments with lower molecular weights as well as ozone [Kohno et al., 1998; Futamura et al., 1999; Ogata et al., 1999; Mok et al., 2000; Moon and Chae, 2001]. On the other hand, no other hydrocarbon compounds besides toluene and formaldehyde and no ozone were detected in this process. One molecule of toluene can form seven carbon-containing molecules. The black square symbol in Fig. 10 stands for the summation of CO, CO_2 and HCHO concentrations, and the white square symbol indicates seven times the amount of toluene decomposed. As observed, the two results were balanced quite well. In this process, the reason that ozone was not formed can be explained by the following equations [Atkinson et al., 1992]:

$$O+O_2 \rightarrow O_3 \quad k_1=5.6\times10^{-34}(300/T)^{2.8}[N_2]\ (cm^3molecule^{-1}s^{-1}) \quad (3)$$

$$O+O_3 \rightarrow 2O_2 \quad k_2=8.0\times10^{-12}\exp(-2060/T)\ (cm^3molecule^{-1}s^{-1}) \quad (4)$$

According to Eqs. (3) and (4), the formation of ozone is in inverse proportion to the temperature while the destruction of ozone is proportional to the temperature. Therefore, it is natural that the formation of ozone should not occur in this process operated at high temperature. As presented in Fig. 10, negligible amount of formaldehyde was observed, regardless of the initial toluene concentration. This result may also be interpreted by the high gas temperature. Actually, formaldehyde can be generated as an intermediate compound during the decomposition process, but it is oxidized to carbon oxides fast at high temperature. The other carbon-containing byproducts observed were carbon monoxide and carbon dioxide. In case of thermal incineration, the following two-stage reaction scheme was suggested to express the decomposition of organic compounds although the real mechanism in detail is more complicated [Cooper and Alley, 1994]:

$$C_xH_y+\left(\frac{x}{2}+\frac{y}{4}\right)O_2 \xrightarrow{k_3} xCO+\frac{y}{2}H_2O \quad (5)$$

$$CO+\frac{1}{2}O_2 \xrightarrow{k_4} CO_2 \quad (6)$$

Eqs. (5) and (6) indicate that organic compound is first converted into CO, and then CO is further oxidized to CO_2. In case of non-thermal plasma process, however, it has been reported that the generation of CO goes via different pathways from that of CO_2 [Futamura et al., 1999; Song et al., 2000]. As mentioned above, this microwave plasma system can decompose organic compounds by both thermal and ionic reactions. Whatever the generation pathways are, CO can be oxidized to CO_2 at high temperature in the presence of oxygen. This can account for the reason that the resulting concentration of CO_2 was much higher than that of CO. In this process, the ratio of CO to CO_2 was very small in the range of 0.06 to 0.19.

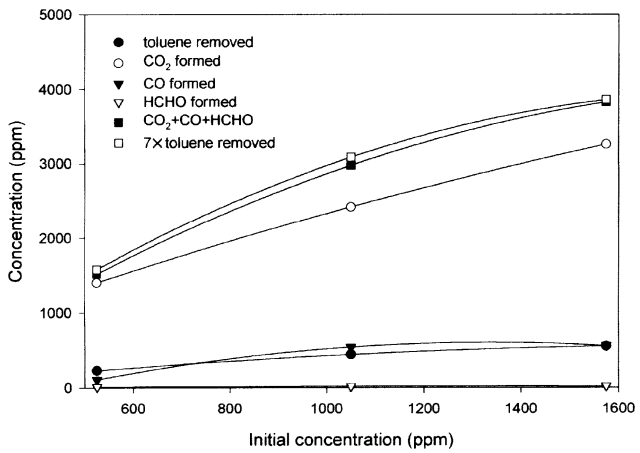

Fig. 10. Byproducts formation in the plasma reactor (feed gas: 10 L/min).

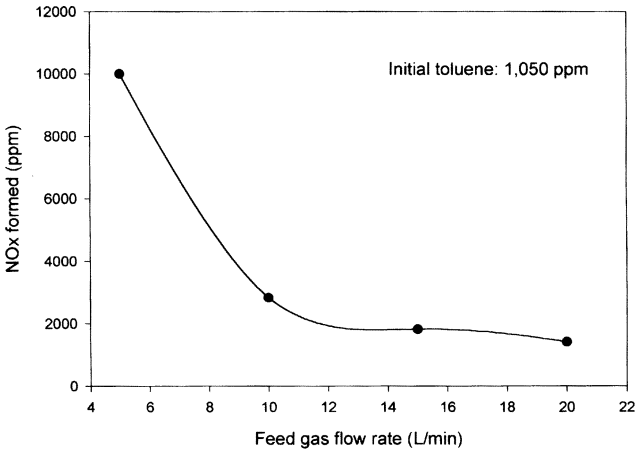

Fig. 11. Formation of nitrogen oxides as a function of feed gas flow rate.

However, in a typical non-thermal plasma reactor, this ratio was about 0.6 at 20% (v/v) oxygen content [Ogata et al., 1999].

This microwave plasma process is operated at high temperature, so that formation of nitrogen oxides is possible. Fig. 11 represents the concentration of NO_x generated in this process. As can be seen, about 10,000 ppm of NO_x ($NO+NO_2$) was generated at a flow rate of 5 L/min, and it decreased to 1,500-2,000 ppm as the flow rate increased to 10-20 L/min. The high concentration of NO_x formed is easily understood by the high gas temperature. Therefore, this process can be valuable only when it is used to treat more harmful compounds such as perfluorocarbons than nitrogen oxides, although this study investigated the decomposition of common volatile organic compound.

As shown above, the decomposition efficiency was not so high when air was used as the background gas. Nitrogen in air shifts the electron energy density distribution to less favorable conditions for the formation of active species [Snyder and Anderson, 1998]. In nitrogen mixtures, a large fraction of electron energy is lost due to vibrational excitation and dissociation of N_2 molecules [Kucukarpaci, 1979], giving less ionic species to participate in the decomposition. To improve the decomposition efficiency, argon was used to assist plasma generation. When argon is used as the background gas, such losses of electron energy as mentioned above do not occur, and thus it is suitable for the purpose of assisting the generation of high density plasma. First, the experiment was conducted by using argon only as the background gas. After that, both air and argon were used as the background gas. One experiment was performed by injecting 5 L/min of argon into the side holes of the nozzle while 5 L/min of air containing toluene was fed to the center hole of the nozzle. The other experiment was performed by injecting gases reversely. Fig. 12 presents the effect of argon on the decomposition efficiency of toluene. The initial concentration in the horizontal axis is based on the total flow rate (argon+air). As expected, the decomposition efficiency was largely enhanced by the use of argon. When argon is used as the background gas, a part of toluene can be decomposed by the energetic electron impact dissociations:

$$C_6H_5 \cdot CH_3 + e \xrightarrow{k_5} \text{products} + e \quad (7)$$

where e denotes the energetic electron, and the rate constant is of the order of 10^{-6} cm^3/molecules/s [Kohno et al., 1998]. The additional probable decomposition channels may be the excitation transfer reactions with the excited argon molecules and the charge transfer reactions with argon ions:

$$C_6H_5 \cdot CH_3 + Ar^* \xrightarrow{k_6} \text{products} + Ar \quad (8)$$

$$C_6H_5 \cdot CH_3 + Ar^+ \xrightarrow{k_7} \text{products} + Ar \quad (9)$$

where Ar^* and Ar^+ stand for the excited molecule and ion, respectively. The energy yield (energy consumption/toluene molecule decomposed) is dependent on the initial concentration and the microwave power. When the initial concentration was 1,575 ppm and the microwave power was 850 W, for instance, 62% decomposition efficiency was obtained with argon-toluene mixture. This decomposition efficiency is tantamount to an energy yield of 1,337 eV per toluene molecule decomposed. Meanwhile, Krasnoperov et al. [1997] reported that conventional non-thermal plasma process using dielectric barrier discharge requires electrical energy in the range of 505-1,980 eV to decompose one molecule of toluene. When argon was injected into the side holes of the nozzle, almost similar decomposition efficiency to the case that argon was injected to the center hole of the nozzle was shown. In case of trichloroethylene (1,000 ppm), about 80% decomposition efficiency was obtained by feeding 5 L/min of argon to the side nozzles with the total flow rate kept 10 L/min. This decomposition efficiency is much higher than the 53% obtained by using air alone as the background gas. Rosocha et al. [1993] presents the rate constant data for the electron impact dissociation of molecular oxygen to form atomic oxygen for the argon and air combination. The rate of atomic oxygen produced in the air-like mixture is approximately an order of magnitude less than the rate of atomic oxygen produced in the argon mixture. Since atomic oxygen is one of the active species utilized for the decomposition of trichloroethylene [Rosocha et al., 1993], the decomposition efficiency in air alone differs from that in air-argon mixture. Argon can also affect the rate of generation of other active species related to the decomposition of trichloroethylene in a similar way. Collectively, the presence of argon enhances the decomposition efficiency of organic compounds. Argon in the treated gas stream can be separated and recycled upstream for repeated use.

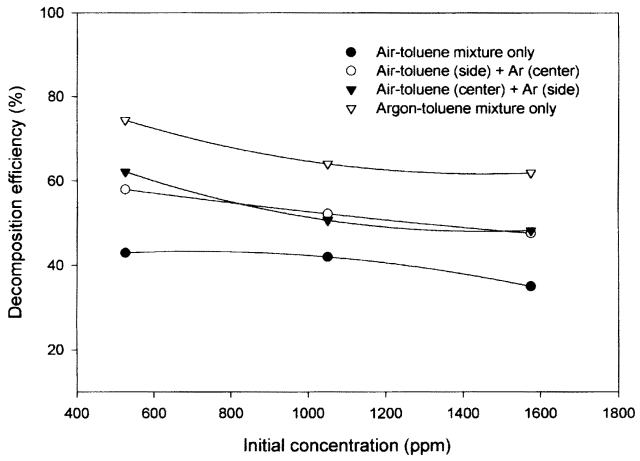

Fig. 12. Effect of argon on the decomposition of toluene.

To decompose organic compounds effectively, the feed gas flow should be concentrated into the plasma flame. Otherwise, the decomposition efficiency of organic compounds will not be high. In the present system, the plasma flame quivered a little and frequently leaned, probably because of the presence of the spark igniter. For practical applications, therefore, the microwave plasma system should be able to produce and sustain plasma without the help of a spark igniter. One method to produce plasma without using a spark igniter is to apply dc high voltage to the cathode of magnetron instead of half-wave rectified voltage [Bae et al., 2002], which makes it possible to obtain continuous microwave power. The application of the continuous microwave power to the decomposition of organic compounds is left as a topic for further study.

CONCLUSIONS

A microwave-sustained atmospheric pressure plasma system based on a waveguide was used to decompose volatile organic compounds. A magnetron detached from a household microwave oven was used

as the microwave source. For a nozzle tip diameter of 10.2 mm and hole diameter of 38.0 mm, the reflection of microwaves was minimized when the position of the nozzle center was 20 mm apart from the short. The decomposition of toluene largely decreased with the increase in the feed gas flow rate due to the decreased gas temperature and the decreased concentrations of active species available, whereas it was not a strong function of the initial concentration. In the application of this plasma system to the decomposition of organic compounds, argon may be used as a gas assisting plasma generation. When argon and the feed gas were injected to the side holes and the center hole of the nozzle and vice versa, large enhancement in the decomposition of organic compounds such as toluene and trichloroethylene was achieved. The principal byproduct was nitrogen oxides because this system was operated at high temperature, but operation at high temperature resulted in much higher CO_2/CO ratio, compared to the non-thermal plasma process using high voltage. Since only few studies on microwave plasma process have been conducted so far, the results obtained in this study may throw some light on further development of this process.

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NOMENCLATURE

a : width of wide waveguide wall [cm]
c : speed of light [cm/s]
c_p : molar heat capacity [cal/mol/K]
e : energetic electron
f : frequency of microwave [Hz]
k_1-k_4 : reaction rate constant [cm^3/molecules/s]
$\dot{m}$: molar flow rate of feed gas [mol/s]
PF : forward microwave power [W]
PR : reflected microwave power [W]
T_1 : temperature of feed gas entering the nozzle [K]
T_2 : final temperature [K]

Greek Letters

α : coefficient in Eq. (2)
β : coefficient in Eq. (2)
γ : coefficient in Eq. (2)
λ : free space wavelength [cm]
λ_g : guide wavelength [cm]

REFERENCES

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson Jr., R. F., Kerr, J. A. and Troe, J., "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV," *J. Phys. Chem. Ref. Data*, **21**(6), 1125 (1992).

Bae, Y. S., Choi, E. M., Chung, W. S., Lee, Y. H., Namkung, W. and Cho, M. H., "Development of 2.45 GHz Waveguide-Based Air Torch System," Joint Int. Plasma Symp. 6th APCPST, 15th SPSM, OS2002 and 11th KAPRA, Lotte Hotel, Jeju, South Korea, July 1-4 (2002).

Baeva, M., Gier, H., Pott, A. and Uhlenbusch, J., "Studies on Gas Purification by a Pulsed Microwave Discharge at 2.46 GHz in Mixtures of N_2/NO/O_2 at Atmospheric Pressure," *Plasma Chem. Plasma Proc.*, **21**, 225 (2001).

Bailin, L. J., Sibert, M. E., Jonas, L. A. and Bell, A. T., "Microwave Decomposition of Toxic Vapor Simulants," *Environ. Sci. Technol.*, **9**, 254 (1975).

Cho, W., Baek, Y., Pang, H., Kim, Y. C. and Moon, S., "A Study on Conversion of Methane to C2+ Hydrocarbons by a Microwave Plasma," *J. Korean Ind. Eng. Chem.*, **9**(1), 94 (1998a).

Cho, W., Baek, Y., Pang, H. and Kim, Y. C., "A Direct Catalytic Conversion of Natural Gas to C2+ Hydrocarbons by a Microwave Plasma," *Korean J. Chem. Eng.*, **15**, 500 (1998b).

Cho, S. J., Ryoo, M. W., Soun, K. S., Lee, J. H. and Kang, S. K., "A Catalytic Combustion Technology of Concentrated VOCs in Textile Coating Process," *Korean J. Chem. Eng.*, **16**, 478 (1999).

Choi, Y. S., Song, Y. H., Kim, S. J. and Kim, B. U., "A Study on the Toluene Decomposition Using an Adsorptive Dielectric Discharge Plasma," *HWAHAK KONGHAK*, **38**, 423 (2000).

Cooper, C. D. and Alley, F. C., "Air Pollution Control: A Design Approach," Waveland Press, Inc. (1994).

Futamura, S., Zhang, A. and Yamamoto, T., "Mechanisms for Formation of Inorganic Byproducts in Plasma Chemical Processing of Hazardous Air Pollutants," *IEEE Trans. Ind. Appl.*, **35**(4), 760 (1999).

Jeong, H. K., Kim, S. C., Han, C., Lee, H., Song, H. K. and Na, B. K., "Conversion of Methane to Higher Hydrocarbons in Pulsed DC Barrier Discharge at Atmospheric Pressure," *Korean J. Chem. Eng.*, **18**, 196 (2001).

Kim, J. S. and Lee, T. K., "Effect of Humidity on the Photocatalytic Degradation of Trichloroethylene in Gas Phase over TiO_2 Thin Films Treated by Different Conditions," *Korean J. Chem. Eng.*, **18**, 935 (2001).

Kim, S. J., Cho, S. Y. and Kim, T. Y., "Adsorption of Chlorinated Volatile Organic Compounds in a Fixed Bed of Activated Carbon," *Korean J. Chem. Eng.*, **19**, 61 (2002).

Kohno, H., Berezin, A. A., Chang, J. S., Tamura, M., Yamamoto, T., Shibuya, A. and Honda, S., "Destruction of Volatile Organic Compounds Used in a Semiconductor Industry by a Capillary Tube Discharge Reactor," *IEEE Trans. Ind. Appl.*, **34**(5), 953 (1998).

Krasnoperov, L. N., Krishtopa, L. G. and Bozzelli, J. W., "Study of Volatile Organic Compounds Destruction by Dielectric Barrier Corona Discharge," *J. Adv. Oxid. Technol.*, **2**(1), 248 (1997).

Kucukarpaci, H. and Lucas, J., "Simulation of Electron Swarm Parameters in Carbon Dioxide and Nitrogen for High E/N," *J. Phys. D*, **12**, 2123 (1979).

Mok, Y. S., Kim, J. H., Ham, S. W. and Nam, I., "Removal of NO and Formation of Byproducts in a Positive Pulsed Corona Discharge Reactor," *Ind. Eng. Chem., Res.*, **39**(10), 3938 (2000).

Mok, Y. S., Nam, C. M., Cho, M. H. and Nam, I., "Decomposition of Volatile Organic Compounds and Nitric Oxide by Non-Thermal Plasma Discharge Processes," *IEEE Trans. Plasma Sci.*, **30**(1), 408 (2002).

Moon, S. and Chae, J., "A Study on Toluene Removal by Characteristics of Pulse Discharge," *J. Korean Soc. Environ. Eng.*, **23**(2), 243 (2001).

Oda, T., Yamashita, R., Haga, I., Takahashi, T. and Masuda, S., "Decomposition of Gaseous Organic Contaminants by Surface Discharge Induced Plasma Chemical Processing-SPCP," *IEEE Trans.*

Ind. Appl., **32**(1), 118 (1996).

Ogata, A., Shintani, N., Mizuno, A., Kushiyama, S. and Yamamoto, T., "Decomposition of Benzene Using a Nonthermal Plasma Reactor Packed with Ferroelectric Pellets," *IEEE Trans. Ind. Appl.*, **35**(4), 753 (1999).

Park, H. K., "Microwave Engineering," 3rd Ed., Hee Jung Dang Press (1991).

Rosocha, L. A., Anderson, G. K., Bechtold, L. A., Coogan, J. J., Heck, H. G., Kang, M., McCulla, W. H., Tennant, R. A. and Wantuck, P. J., "Treatment of Hazardous Organic Wastes Using Silent Discharge Plasmas," Non-Thermal Plasma Techniques for Pollution Control: Part B, Springer-Verlag, Berlin, Germany, 281 (1993).

Sieck, L. W., Buckley, T. J., Herron, J. T. and Green, D. S., "Pulsed Electron-Beam Ionization of Humid Air and Humid Air/Toluene Mixture: Time-Resolved Cationic Kinetics and Comparisons with Models," *Plasma Chem. Plasma Proc.*, **21**(3), 441 (2001).

Snyder, H. R. and Anderson, G. K., "Effect of Air and Oxygen Content on the Dielectric Barrier Discharge Decomposition of Chlorobenzene," *IEEE Trans. Plasma Sci.*, **26**(6), 1695 (1998).

Song, J. H., Seo, K. W., Mok, Y. I., Park, K. Y. and Ahn, B. S., "Catalytic Hydrogenolysis of CFC-12 (CCl_2F_2) over Bimetallic Palladium Catalysts Supported on Activated Carbon," *Korean J. Chem. Eng.*, **19**, 246 (2002).

Song, Y., Shin, D., Shin, W., Kim, K., Choi, Y., Choi, Y. S., Lee, W. and Kim, S., "Characteristics of Non-Thermal Plasma Processes for Air Pollution Control," *J. Korean Soc. Atmospheric Envron.*, **16**(3), 247 (2000).

Uhm, H. S., "Contamination Control of Emission Discharge," US Patent 5,830,328 (1998).

von Hagen, J., Venot, Y., Zhang, Y. and Wiesbeck, W., "Microwave-Generated Plasma in Air Under Standard Conditions," *IEEE Trans. Plasma Sci.*, **29**(4), 604 (2001).

Wojtowicz, M. A., Miknis, F. P., Grimes, R. W., Smith, W. W. and Serio, M. A., "Control of Nitric Oxide, Nitrous Oxide, and Ammonia Emissions Using Microwave Plasmas," *J. Hazardous Materials*, **74**, 81 (2000).

Yan, K., Hui, H., Cui, M., Miao, J., Wu, X., Bao, C. and Li, R., "Corona-Induced Non-Thermal Plasmas: Fundamental Study and Industrial Applications," *J. Electrostatics*, **44**, 17 (1998).