

Photo-catalytic destruction of ethylene using microwave discharge electrodeless lamp

Do-Jin Lee*, Young-Kwon Park**, Sun-Jae Kim***, Heon Lee****, and Sang-Chul Jung****,†

*Department of Agricultural Education, Sunchon National University, Sunchon, Jeonnam 540-742, Korea

**School of Environmental Engineering, University of Seoul, Seoul 130-743, Korea

***Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, Korea

****Department of Environmental Engineering, Sunchon National University, Sunchon, Jeonnam 540-742, Korea

(Received 18 June 2014 • accepted 4 November 2014)

Abstract—A double tube type microwave discharge electrodeless lamp was employed to investigate the photo-catalytic decomposition of ethylene gas, an important VOC species. The anatase TiO_2 film photo-catalyst balls prepared by a low pressure metal organic chemical vapor deposition method were used. In addition, the advantages of microwave/UV/ TiO_2 photo-catalysts hybrid process were analyzed. The removal performance was examined under different conditions with different initial ethylene concentrations, gas residence times and oxygen concentrations. At all microwave powers tested, UV-C exhibited much larger irradiance than UV-A and UV-B. The degradation efficiency of ethylene increased with increasing microwave intensity, with decreasing inlet concentration, and with decreasing reaction gas flow rate. Taking the energy cost into account, residence time should be determined considering inlet concentration, volume of degradation, capacity of devices, and admitted costs. Microwave intensity was shown to be a critical operation variable for the photo-catalytic degradation of ethylene, required to be determined depending on initial ethylene concentration.

Keywords: Ethylene, Microwave, Electrodeless Lamp, TiO_2 , UV

INTRODUCTION

Ethylene gas (C_2H_4) is beneficially used in many instances, such as the promotion of uniform ripening in bananas and de-greening of fresh citrus, but the effects of ethylene gas are not all positive. Even small amounts in the atmosphere in a storage facility can induce undesirable reactions in most fresh produce, such as development of senescence, bitter flavors, chlorophyll loss, disease susceptibility, and physiological disorders. Removal of ethylene from the storage environment retards spoilage, reduces loss, and increases profit. While conventional methods such as venting, potassium permanganate oxidation, adsorption onto brominated carbon, catalytic oxidizers, and hypobaric storage help to control and remove ethylene from storage facilities, each has limitations in controlling ethylene levels in the presence of highly ethylene-yielding process and can result in the alteration of temperature and humidity conditions in the storage facilities [1]. Photo-catalysis using titanium dioxide (TiO_2) as the catalyst is seen as a promising alternative to the oxidation processes used to degrade ethylene in most conventional methods and has attracted considerable attention [2-5]. The photo-catalytic degradation of ethylene using TiO_2 can be carried out under high humidity at both room temperature and low temperature [6]. The major advantage is the complete mineralization of undesirable organic contaminants in gas phases to CO_2 and H_2O in addition to the chemical stability of the catalyst, which is also non-toxic and inexpensive [7,8].

Microwave energy has been increasingly used in synthetic organic chemistry because of its capacity to accelerate reactions and to improve yields and selectivity [9]. There is growing interest in using microwave radiation to drive or otherwise assist chemical reactions. Various types of organic and inorganic reactions, once performed using classical heating methods, are now routinely performed using microwave radiation [10]. Recently, researches have been conducted actively to improve oxidative degradation performance by adding microwave irradiation as an effort to utilize TiO_2 photo-catalyst treatment more efficiently [11-13].

A double tube type microwave discharge electrodeless lamp (MDEL) that emits UV upon the irradiation of microwave was developed and has been applied to photo-catalytic decomposition of various pollutants [14]. Therefore, it will be interesting to study photo-oxidation of C_2H_4 in the gas phase using MDEL to demonstrate the effect of microwave condition. Furthermore, photo-catalytic oxidation of C_2H_4 was also studied using microwave/UV/ TiO_2 hybrid process for comparison. The result obtained is presented in this manuscript.

MATERIAL AND METHODS

1. Microwave/UV/ TiO_2 Photo-catalysts Hybrid System

The microwave/UV/ TiO_2 experimental apparatus used in this study (Fig. 1) consists of microwave irradiation equipment, an MDEL, a quartz reactor tube (230 mm length, 40 mm diameter) in which photo-degradation of ethylene gas takes place, a gas flow control system using a mass flow controller. The microwave irradiation equipment, manufactured by Korea Microwave Instrument Co., consisted of a microwave generator (frequency, 2.45 GHz; maxi-

†To whom correspondence should be addressed.

E-mail: jsc@sunchon.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

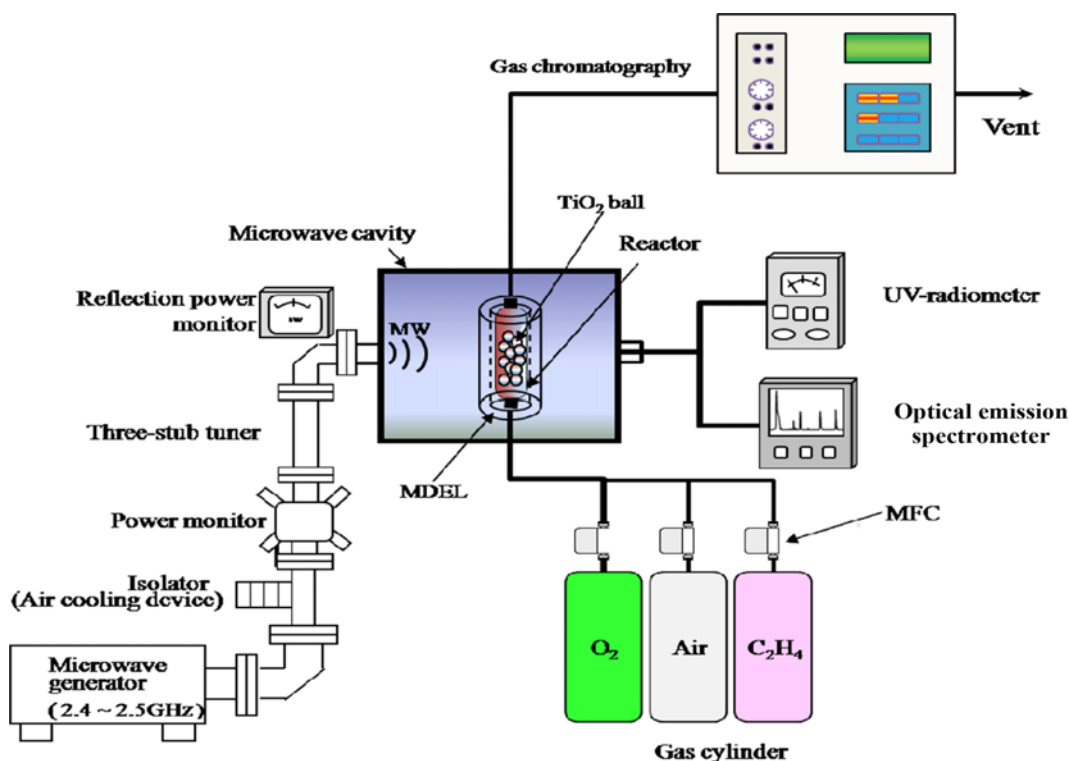


Fig. 1. Schematic diagram of the microwave/UV/TiO₂ photo-catalyst experimental apparatus.

mal power, 1 kW), a three-stub tuner, a power monitor, and a reaction cavity. Microwave radiation used to irradiate the reaction gas flow was delivered through a wave-guide. Microwave irradiation was continuous and the microwave intensity was adjusted by using a connected power monitor. Optimal low reflection of the microwave radiation was achieved with the three-stub tuner. UV-meter sensors and the microwave generator were located on the right-hand side and left-hand side of the microwave cavity, respectively. A stirrer was installed on the back side in the reaction cavity (Fig. 1) to enhance the transfer of microwave.

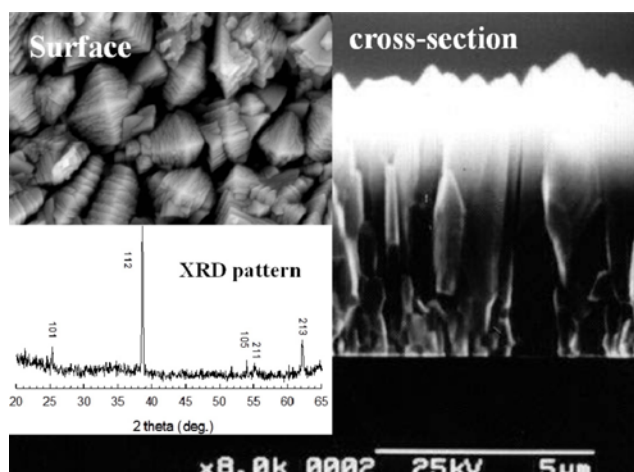


Fig. 2. SEM images and X-ray diffraction pattern of the TiO₂ film prepared using the CVD method at 1 torr and 773 K.

2. TiO₂ Photo-catalyst Balls

TiO₂ photo-catalyst balls used were prepared using a low pressure metal organic chemical vapor deposition (LPMOCVD) method. Titanium tetraisopropoxide (Ti(OC₃H₇)₄, TTIP) was used as the precursor to generate a TiO₂ film on alumina balls (Nikkto, HD-11) with 8-mm diameter. Details of the apparatus and prepared method were described in our previous paper [15]. Fig. 2 shows scanning electron microscope (SEM) images and X-ray diffraction pattern of the prepared TiO₂ film. The diffraction pattern confirms that 112 face-oriented anatase crystal structure TiO₂ films were prepared. The SEM image shows very fine particles and very densely packed columnar crystals. Anatase TiO₂ films were prepared on the alumina balls with a thickness of 5-8 μm indicate X-ray diffraction pattern and SEM.

3. Double Tube Type MDEL

TiO₂ photo-catalysts are excited by UV light, producing strong oxidants that can degrade organic compounds. Therefore, provision of UV is essential for the use of TiO₂ photo-catalysts. Typical UV lamps, however, have metal electrodes that prevent them from being used in the microwave-irradiation equipment. Therefore, a double tube type MDEL (170-mm length, 36-mm inner diameter, 55-mm outer diameter) that emits UV upon the irradiation of microwave from plasma state was developed in this study. It was made of quartz to maximize the reaction efficiency. A small amount of mercury gas was doped between the tubes inside the double tube UV lamp that was kept vacuumed. The lamp used in this study is UV-C type lamp, although UV-A and UV-B wavelength lights are emitted as well. Fig. 3 shows a photograph of the MDEL used in this study (a) and a snapshot of the lamp emitting UV light by

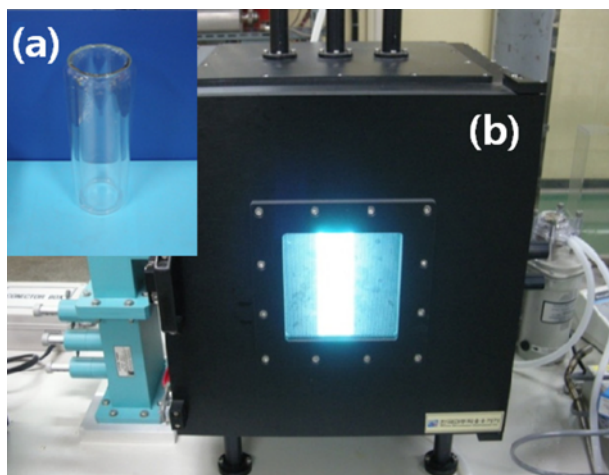


Fig. 3. Photographs of the MDEPL (a) and microwave-discharged lamp set in the microwave oven (b).

microwave irradiation in the microwave oven (b).

4. Evaluation of Reaction Activity

Experiments were performed to evaluate the microwave-assisted photo-catalytic degradation of ethylene (PS chemical Co., 99.95%) gas by using a flow type reactor under atmospheric pressure. The reactant gas was diluted with air and oxygen at the inlet of the reactor tube. Mass-flow controllers modulated the flow rates of carrier gases. The total flow rate of gas fed into the reactor was 500-1,000 cc/min and the oxygen concentration in the gas varied 20 and 100 mol%. The decomposition rate was calculated from the difference between the ethylene concentrations measured at the reactor inlet and outlet as a function of residence time. The reactant gas was analyzed by gas chromatography (DS-6200, Donam Instrument Co.) with a porapak N (7'x1/8", Alltech) column and an FID (flame ionization detector). The oven temperature was programmed to change from 313 K (5 min) to 433 K (3 min), at a heating rate of 10 °C/min. The concentration of ethylene was obtained from the GC peak areas before and after reaction to calculate the decomposition rate.

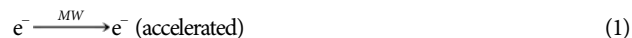
RESULTS AND DISCUSSION

1. Characteristics of the MDEL

Microwave discharge electrodeless plasma lamps (MDELs), a unique light source, were first reported in 1968 [16]. The principle involved is the absorption of high-frequency electromagnetic waves produced by a microwave generator by noble gases and vaporizable elements in the plasma state lamp, which results in UV emission. Mercury, sodium, sulfur, selenium, and cadmium can be used as vaporizable elements, whereas the noble gases are generally argon, neon, and krypton, among others. Compared with normal UV light sources, due to the absence of electrodes, MDELs do not produce blackened electrodes caused by wear and tear, oxidation, and sealing. In addition, MDELs have many advantages such as low price, low energy cost, high light intensity, and simple reactor. There are many options for light-emitting materials, so MDELs can provide different wavelengths of UV radiation [17]. They have been applied

to disinfection of drinking water and degradation of pollutants in water [18]. However, research on degradation of gaseous pollutants with MDEL is still scarcely reported.

A microwave field can trigger gas discharge causing the emission of UV/Vis radiation. This phenomenon has been studied for many years and is well understood. The theory of Hg-MDEL operation, as it is currently understood, is shown in Eqs. (1) through (5).



Free electrons in the fill (i.e., electrons that have become separated from the environment because of the ambient energy) accelerate as a result of the microwave field energy [19]. They collide with the argon atoms and ionize them to release more electrons. The repetitive effect causes the number of electrons to increase significantly over a short period of time, an effect known as an “avalanche.” The energetic electrons collide with the heavy-atom particles (argon or mercury) present in the plasma, exciting them from a ground state to higher energy levels. The excitation energy is then released as UV/Vis radiation with spectral characteristics that depend on the composition of the envelope. The excited molecular or atomic species in the plasma can emit photons over very broad portion of the electromagnetic spectrum, ranging from x-ray to the infrared ray. The MDEL employed in this study has a stronger intensity than common mercury lamps, especially in UV range. The ultraviolet and visible wavelengths emitted were detected by UV/Vis-spectrometer (AVASPEC-2048, Avantes Co. Ltd.). The sensor of the UV/Vis-spectrometer was installed on the right-hand-side port of the microwave cavity. The distance between MDEL and the sensor was about 30 cm. The emission wavelengths of MDEL distributed widely in the range of 180-600 nm: 254, 297, 311, 365, 404, 435, 547 and 579 nm. The MDEL containing a mixture of mercury and argon showed mainly atomic Hg emission lines at 253.7 nm

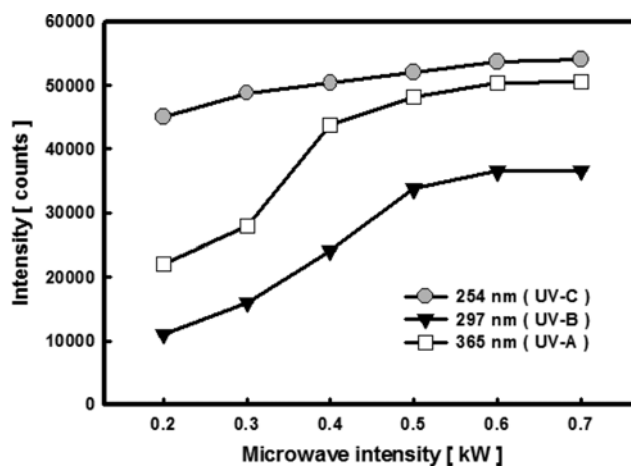


Fig. 4. Change of the UV intensities radiated at different microwave intensities.

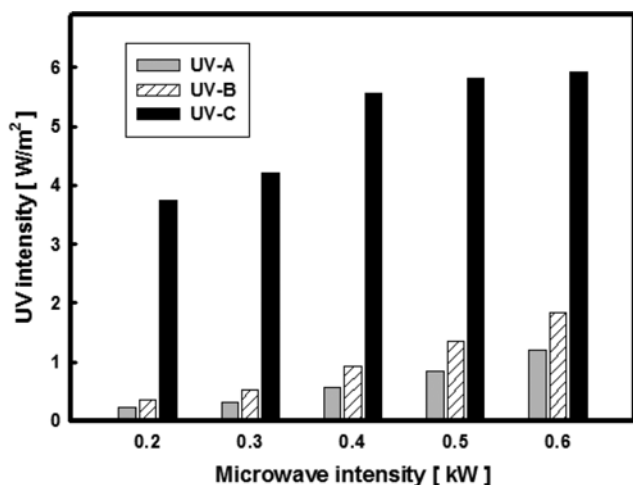


Fig. 5. Comparison of the UV irradiances measured at different microwave intensities.

($6^2P_1-6^2S_0$). The influence of microwave power on the UV spectrum emitted from the MEDL was examined. Fig. 4 shows the UV spectrum emitted from MDEPL with different input microwave intensities measured. UV-C (254 nm) intensity was high even at the lowest power (0.2 kW), increasing slowly with the input microwave power. However, the intensities of UV-A (365 nm) and UV-B (297 nm) were very low at low input microwave power, but they increased rapidly with increasing microwave power. All the three UV waves showed little change in their intensity above 0.6 kW of microwave power.

Another measurement made in this study was the irradiance (W/m^2) at each UV wavelength range. A UV radiometer (HD2102-2, Delta OHM) was used to measure this quantity. Fig. 5 compares the UV irradiance measured at different microwave intensities. The sensor of the UV radiometer was installed on the right-hand-side port of the microwave cavity (Fig. 1). The distance between MDEL and the sensor was about 30 cm. The ranges of wavelength detected by UV-A, UV-B, and UV-C sensors are 315–400 nm, 280–315 nm, and 220–280 nm, respectively. From Fig. 5, the UV irradiation from the MDEL used in this study is dominated by short-wave UV with high energy. At all microwave intensities tested in this study, UV-C exhibited much larger irradiance than UV-A and UV-B. The UV-A and UV-B irradiances increased with the microwave power, whereas the UV-C energy showed little change at microwave power larger than 0.4 kW. This result is in agreement with the result shown in Fig. 4. In the meantime, the irradiances of UV-A and UV-B increased with increasing microwave power, which is not consistent with the result shown in Fig. 4 in which UV intensity did not change much when the microwave power was larger than 0.5 kW. This is probably because the UV/Vis-spectrometer measurement of UV-A and UV-B shown in Fig. 4 was made at single wavelengths of 365 nm and 297 nm, whereas the UV radiometer measurement of UV-A and UV-B shown in Fig. 5 was made for wavelength ranges of 315–400 nm and 280–315 nm.

2. Photo-degradation and Photo-catalytic Degradation of Ethylene

Fig. 6 compares the ethylene removal efficiency obtained at dif-

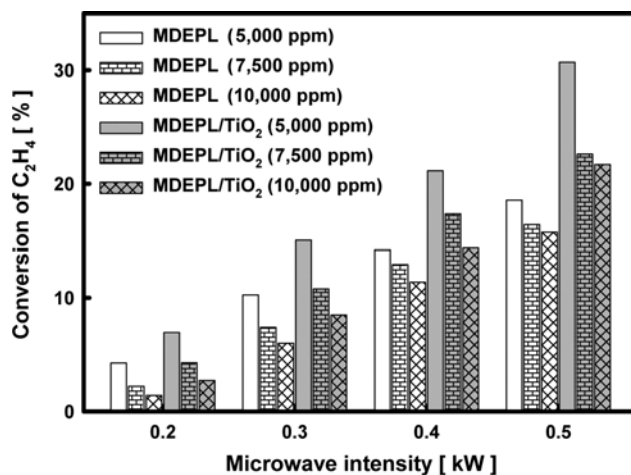


Fig. 6. Photodegradation and photo-catalytic degradation of ethylene at various initial concentrations.

ferent initial concentrations by photodegradation, which uses MDEL only, and by photo-catalytic degradation, which uses MDEL and TiO_2 photo-catalysts together. The initial ethylene concentration was 5,000–10,000 ppm. Air was used as the carrier gas. The total inlet flow rate was 1,000 cc/min. At every experimental condition, the ethylene removal efficiency increased with increasing microwave intensity. In addition, the removal efficiency decreased with increasing initial ethylene concentration in both photodegradation and photocatalytic degradation. Generally, photocatalysis is known to exert high efficiency at low concentrations [20], which agrees with the result of this study. Meanwhile, the ethylene removal efficiency of photocatalytic degradation was higher by 20–30% than that of photodegradation. For most volatile organic compounds (VOCs), including ethylene, if the initial concentration is sufficiently high, photocatalyst surface becomes saturated with VOCs so quickly that it is not affected by the initial VOC concentration. Therefore, the photocatalytic degradation of VOCs is first-order reaction whose rate is proportional to VOC concentration when the concentra-

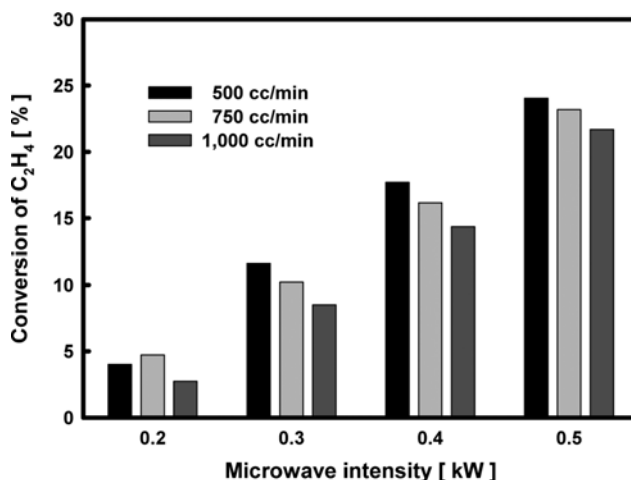


Fig. 7. Photo-catalytic degradation of ethylene on various gas flow rate.

tion is low, whereas it is zeroth-order reaction whose rate is independent of VOC concentration when the concentration is high [21].

3. Effect of Gas Flow Rate

Reactor residence time, which is determined by the gas flow rate, is the duration of stay in the reactor (from the entry and to the exit) of exhaust gas. The results shown in Fig. 7 were achieved with the inlet ethylene concentration of 10,000 ppm and the reaction gas was diluted with air. As presented, with the flow rate increased from 500 cc/min to 1,000 cc/min, the decomposition efficiency of ethylene decreased, caused by decrease in both collision time and collision possibility. Therefore, gas residence time is a key point of photocatalytic decomposition in the experiments. Generally, a longer residence time results in a higher removal efficiency. However, if the residence time is too long, the amount of exhaust gas treated in unit time decreases, which results in a low energy efficiency and high energy cost. Therefore, when microwave/UV/TiO₂ photo-catalysts hybrid process is used, the residence time should be determined by comprehensively taking into account the inlet concentration, volume of degradation, capacity of devices, and admitted costs.

4. Effect of Oxygen Concentration

The influence of concentration of oxygen, which plays a role as an oxidant in the photo-catalytic removal of ethylene, on the removal efficiency was also investigated in this study. Fig. 8 shows the removal efficiency obtained with different carrier gas as a function of microwave power. Air, composed of 20% oxygen and 80% nitrogen, and oxygen were used, separately, as the carrier gas. The total gas flow rate was controlled at 1,000 cc/min. The inlet ethylene concentration was 5,000-10,000 ppm. The ethylene removal efficiency increased with increasing microwave intensity and decreasing initial ethylene concentration at every experimental condition. The removal efficiency was higher only by 1-5% when oxygen was used as the carrier gas than when air was used. This result is in good agreement with a previous study in which the photocatalytic degradation rate of VOCs increased with increasing oxygen concentration [22]. This was attributed to the scavenging of electrons formed on the surface of TiO₂ by oxygen, which is an electron acceptor that receives electrons fast to be reduced, suppressing the recombi-

nation of electrons and holes and thereby increasing the overall reaction rate. The formation of superoxide (O₂⁻) ion by the combination of oxygen and electron also promotes, via several steps, the production of OH radicals, leading to increased reaction rate. This indicates that 20% oxygen is enough to promote the photocatalytic degradation of ethylene using the microwave/UV/TiO₂ photo-catalysts hybrid process. From our results, we conclude that for the photo-catalytic degradation of ethylene the microwave intensity is the critical operation variable required to be determined depending on the initial ethylene concentration, while air can be used as the carrier gas.

CONCLUSIONS

The following conclusions were made from the results of photocatalytic degradation of ethylene using microwave/UV/TiO₂ hybrid process:

- 1) The anatase TiO₂ film photo-catalyst balls prepared by a low pressure metal organic chemical vapor deposition method were used.
- 2) The MDEL used in this study showed atomic Hg emission lines, mainly at 253.7 nm. At all microwave powers tested, UV-C exhibited much larger irradiance than UV-A and UV-B.
- 3) With increasing microwave intensity, the degradation efficiency of ethylene increased, and the degradation efficiency was highest when the inlet concentration was lowest.
- 4) The degradation efficiency of ethylene decreased with the reaction gas flow rate due to increased collision time and collision possibility. Because the energy cost also increases with residence time, the residence time should be determined by comprehensively taking into account the inlet concentration, volume of degradation, capacity of devices, and admitted costs.
- 5) In the photo-catalytic degradation of ethylene, microwave intensity is a critical operation variable required to be determined depending on initial ethylene concentration, while air can be used as the carrier gas.

ACKNOWLEDGEMENT

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2013R1A1A2A10004797).

REFERENCES

1. T. K. Graham, J. N. Veenstra and P. R. Armstrong, *Trans. ASAE*, **41**, 1767 (1998).
2. T. N. Obee and S. O. Hay, *Environ. Sci. Technol.*, **31**, 2034 (1997).
3. T. W. Tibbitts, K. E. Cushman, X. Fu, M. A. Anderson and R. J. Bula, *Adv. Space Res.*, **22**, 1443 (1998).
4. D. R. Park, J. L. Zhang, K. Ikeue, H. Yamashita and M. Anpo, *J. Catal.*, **185**, 114 (1999).
5. K. Surajit, G. F. Andrei and L. G. James, *Appl. Catal. B: Environ.*, **57**, 93 (2005).
6. C. Maneerat, Y. Hayata, N. Egashira, K. Sakamoto, Z. Hamai and M. Kuroyanagi, *Trans. ASAE*, **46**, 725 (2003).

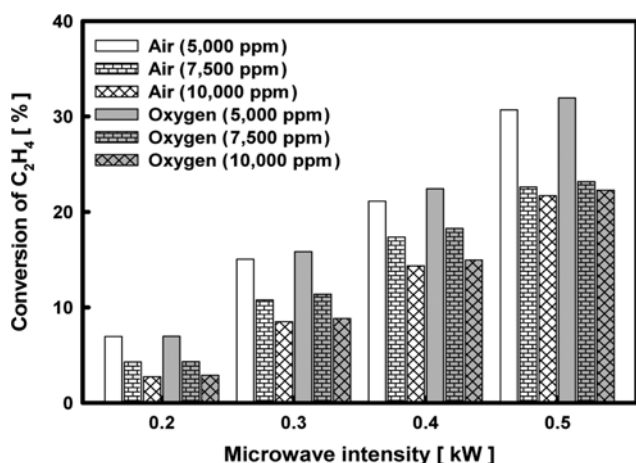


Fig. 8. Effect of carrier gas composition on degradation of HCFC-22.

7. S. C. Jung, S. J. Kim, N. Imaishi and Y. I. Cho, *Appl. Catal. B: Environ.*, **55**, 253 (2005).
8. S. C. Jung, *Korean J. Chem. Eng.*, **25**, 364 (2008).
9. V. Cirkva and M. Hájek, *J. Photochem. Photobiol. A: Chem.*, **123**, 21 (1999).
10. J. Literak and P. Klan, *J. Photochem. Photobiol. A: Chem.*, **137**, 29 (2000).
11. S. Horiyoshi, H. Hidaka and N. Serpone, *J. Photochem. Photobiol. A: Chem.*, **159**, 289 (2003).
12. S. C. Jung, *Water Sci. Technol.*, **63**, 1491 (2011).
13. S. J. Kim, S. C. Kim, S. G. Seo, D. J. Lee, H. Lee, S. H. Park and S. C. Jung, *Catal. Today*, **164**, 384 (2011).
14. S. Horiyoshi, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, **36**, 1357 (2002).
15. S. C. Jung, B. H. Kim, S. J. Kim, N. Imaishi and Y. I. Cho, *Chem. Vap. Deposition*, **11**, 137 (2005).
16. J. M. Mansfiel, M. P. Bratzel, H. O. Norgordo, D. O. Knapp, K. E. Zacha and J. D. Wineford, *Spectrochim. Acta B*, **23**, 389 (1968).
17. P. Muller, P. Klan and V. Cirkva, *J. Photochem. Photobiol. A*, **171**, 51 (2005).
18. C. H. Wu, *Dyes Pigm.*, **77**, 31 (2008).
19. A. Loupy, *Microwaves in organic synthesis*, Wiley-VCH, Weinheim (2006).
20. R. Hoffmann, S. T. Martin, W. Y. Choi and D. W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
21. W. S. Cha, *J. KAIS*, **14**, 1527 (2013).
22. E. Pelizzetti and C. Minero, *Electrochem. Acta*, **38**, 47 (1993).