Global NEST Journal, Vol 10, No 2, pp 249-254, 2008
Copyright© 2008 Global NEST
Printed in Greece. All rights reserved

COMPARISON OF NON-THERMAL PLASMA DECOMPOSITION CHARACTERISTICS OF ORGANO-HALIDE GASES UNDER OXIDIZING AND REDUCING ATMOSPHERE

A. YOKOI[1,*]
T. FUJITA[1]
D. KUCHAR[1]
M. KUBOTA[1]
H. LIWEI[2]
K. USHIROEBISU[3]
H. MATSUDA[1]

[1] Energy Engineering and Science, Nagoya University Furo-cho Chikusa-ku, Nagoya, Aichi, 464-8603, Japan
[2] College of Biological and Environmental Engineering Zhejiang University of Technology Hangzhou, Zhejiang Province, 310027, P.R. China
[3] Engineering Division, Sintokogio Ecotec Company 1, Nishinagane, Sakazaki, Koda-cho, Aichi 444-0104, Japan

Received: 07/11/07
Accepted: 14/12/07

*to whom all correspondence should be addressed:
e-mail: a-yokoi@ees.nagoya-u.ac.jp

ABSTRACT

Halide gases used in various industrial processes significantly contribute to the greenhouse effect owing to their high GWPs. In addition, the halide gases have high chemical stability and thus remain in the atmosphere for a long period. Therefore, effective treatment techniques of halide gases are required to achieve environmental protection. The present work is concerned with the destruction of halide gases such as CF_4, CHF_3 and $CHClF_2$ in a wire-in-tube pulsed corona reactor. In details, the influence of coexisting gases of H_2 and O_2 on non-thermal plasma (NTP) decomposition of CF_4, CHF_3 and $CHClF_2$ was investigated. As a result, decomposition ratios of CF_4 and $CHClF_2$ by NTP were found to be higher under H_2-N_2 atmosphere than under N_2 atmosphere. By contrast, the decomposition ratio of CHF_3 under H_2-N_2 atmosphere was lower than that under N_2 atmosphere. In the case of O_2-N_2 atmosphere, lower decomposition ratios of CF_4, CHF_3 and $CHClF_2$ were obtained under O_2-N_2 atmosphere than under N_2 atmosphere. Additionally, $CHClF_2$ decomposition by NTP in the presence of O_2 yielded the reaction products such as CCl_2F_2, $COCl_2$, COF_2 and CO_2. Then, as the O_2 concentration increased, the formation of undesirable product of CCl_2F_2 decreased, while the generation of CO_2 increased.

KEYWORDS: non-thermal plasma, halide gases, H_2 concentration, O_2 concentration.

1. INTRODUCTION

Greenhouse gases such as CF_4, CHF_3 and $CHClF_2$ are widely used as organic solvents, refrigerants and dry etching agents in semiconductor industry, air conditioners and other industrial processes. However, these gases have high GWPs (Global Warming Potentials), toxicity, and may remain in the atmosphere for a long period, due to their chemical stability (Kataoka, 2001; Mizuno, 2001). Hence, the effective techniques to prevent the release of halide gases into the environment are required.

In the recent years, non-thermal plasma has been noted as one of the prospective techniques for the decomposition of halide gases (Oda *et al.*, 1996; Sathiamoorthy *et al.*, 1999). In non-thermal plasma, the decomposition process starts with dissociation and/or excitation of targeted halide molecules by direct impact of energetic electrons. Further, active radicals such as N, H, O can be formed by dissociation and ionization of background gases. Then, the initiation is followed by so called chain reactions leading to the formation of various

byproducts. The chain reactions between the radicals and halide molecules propagate until stable products are formed.

In our previous study, the plasma decomposition of dichloromethane (CH_2Cl_2) in a pulse corona reactor with and without $Ca(OH)_2$ alkaline absorbent under N_2 and O_2 atmosphere was performed (Huang *et al.*, 2001). During the plasma decomposition of CH_2Cl_2 using a plasma reactor without absorbent, HCl was detected as a byproduct under N_2 atmosphere, while CO, CO_2, $COCl_2$ and NOx were the main byproducts found in the presence of oxygen. By contrast, when the corona reactor was combined with $Ca(OH)_2$ absorbent, HCl and $COCl_2$ were not detected during plasma decomposition of halide gases under O_2 atmosphere. In a subsequent study (Hari *et al.*, 2002), the plasma decomposition of halide gases (CCl_4, SF_6, CHF_3 and $CHClF_2$) in a plasma reactor with/without *in-situ* alkaline absorbent was investigated under N_2 and 2% H_2 atmospheres. At first, without *in-situ* alkaline absorbent, it was found that the decomposition ratios of SF_6, CCl_4 and $CHClF_2$ increased with the addition of 2% H_2 to N_2 compared to those under N_2 atmosphere alone. However, in the case of CHF_3, the decomposition ratio was lower in 2% H_2 atmosphere than that under N_2 atmosphere. Further, when non-thermal plasma was combined with *in-situ* $Ca(OH)_2$ absorption under N_2 and 2% H_2 atmospheres, the decomposition ratios of SF_6, CCl_4 and $CHClF_2$ were higher than those without $Ca(OH)_2$ absorption and products such as HCl, Cl_2, HF and F_2 were found to be effectively removed. The results of these studies indicated that the decomposition of halides and absorption of halogen (Cl and F) were promoted by the formation of hydrogen halides (HCl and HF), and there was an optimum H_2 concentration for the decomposition of halide gases to form hydrogen halides. Therefore, it was of great importance to understand the behavior of plasma decomposition of halides in the presence of H_2 and O_2.

Hence, in this study, non-thermal plasma decomposition of CF_4, CHF_3 and $CHClF_2$ under N_2, H_2-N_2 and O_2-N_2 atmospheres was thoroughly studied. It was considered that, in hydrogen-enriched atmosphere, the halogen atoms are converted to stable hydrogen halides. On the other hand, under O_2-N_2 atmosphere, it was expected that carbon in the structure of halide gases is converted to CO_2 having lower GWP than halide gases.

2. EXPERIMENTAL

In this study, a typical wire-tube combination corona reactor was used for the experiments and the schematic diagram of experimental apparatus is shown in Figure 1.

The reactor consisted of a Pyrex glass tube with an aluminum film attached to the outer wall as the grounding electrode and a coaxial stainless steel wire as the corona wire. Using an AC power source, input voltage (5.0-9.5 kV) was applied to the wire electrode and the experiments were carried out at an input power range of 0.04-0.15 kW and at a fixed frequency of 1.0 kHz. During the experiments, no temperature adjustment was performed and the experiments were conducted at an ambient temperature.

The prepared sample gases of CF_4, CHF_3 or $CHClF_2$ were introduced to the reactor at a fixed flow rate of 200 ml min^{-1} (retention time: 68 s) in all experiments. The concentrations of CF_4, CHF_3 and $CHClF_2$ in all sample gas mixtures were adjusted to 25 ppm or 100 ppm under N_2 gas, and the H_2 or O_2 concentration in the sample gases were adjusted to 0-20,000 ppm. The sample gases before and after the plasma treatment in the reactor were analyzed using an on-line FT-IR (SHIMADZU, FTIR-8700) with a gas cell of 10 cm path length. In the FT-IR measurements, the concentrations of CF_4, CHF_3, $CHClF_2$, HCl, and HF gases were analyzed five times and C_{in}, C_{out}, C_{HCl}, and C_{HF} represent the average values obtained. The decomposition ratio of CF_4, CHF_3, and $CHClF_2$ and the yield of HCl and/or HF from halide decomposition are defined by the following three equations:

$$\text{Decomposition ratio of halides} = \frac{C_{in} - C_{out}}{C_{in}} \quad (1)$$

$$\text{Yield of HCl} = \frac{C_{HCl}}{(C_{in} - C_{out}) \times m} \quad (2)$$

$$\text{Yield of HF} = \frac{C_{HF}}{(C_{in} - C_{out}) \times n} \tag{3}$$

where C_{in} and C_{out} [ppm] are the inlet concentration and the outlet concentration of the halide, C_{HCl} and C_{HF} are the concentrations of HCl and HF in the decomposition products. The letters *m* and *n* are the respective numbers of Cl and F atoms in the halide compounds.

Regarding the decomposition of $CHClF_2$, CO_2 fraction was defined as followed:

$$CO_2 \text{ fraction} = \frac{C_{CO_2}}{(C_{in} - C_{out})} \tag{4}$$

where C_{CO2} is the concentration of CO_2 in the decomposition products.

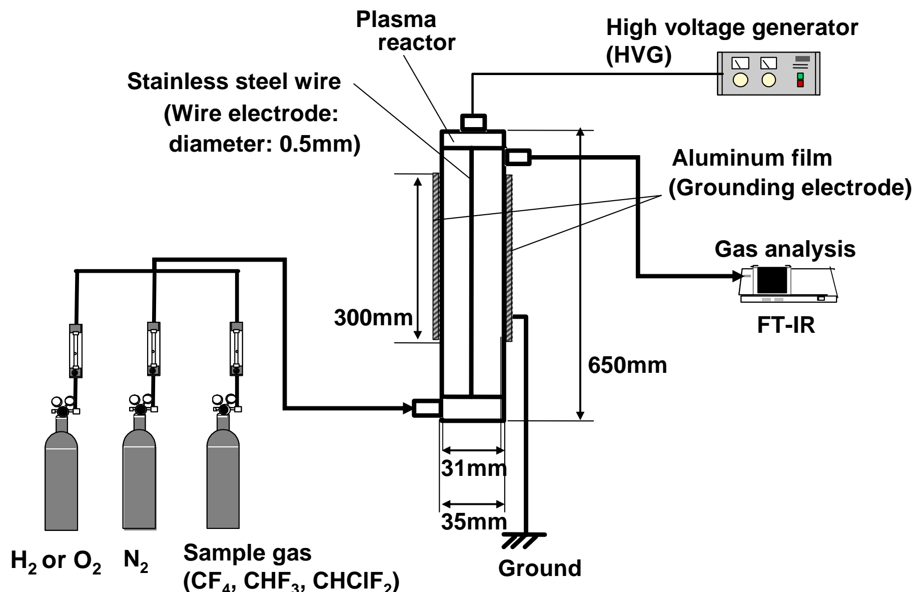

Figure 1. Experimental apparatus

3. RESULTS AND DISCUSSION

3.1. Decomposition of halides by non-thermal plasma under N_2 atmosphere

Figure 2 shows the decomposition of three different halide gases (CF_4, CHF_3 and $CHClF_2$) as a function of power input to the plasma reactor.

As can be seen, the decomposition of halide gases started at input powers above 0.04 kW, and thus it was considered that an input power above 0.04 kW was necessary for the formation of non-thermal plasma with corona discharge in this type of reactor. Further, regarding the type of halide gas used, the decomposition of chlorine containing halide gas of $CHClF_2$ was found to be easier than that of CF_4 and CHF_3. In addition, the decomposition of CF_4 was found to be the most difficult to achieve.

In N_2 gas, the plasma decomposition of halide compounds was most likely initialized by dissociative electron attachment reactions generating chemically active Cl and/or F atoms and followed by a chain of radical reactions to form the final products.

The products of HCl and HF, once formed by halide decomposition, did not participate in further reactions because of the relatively strong H-Cl and H-F bonds. However, the Cl and F atoms produced might have reacted together to form molecular Cl_2 and F_2. Given this, the major end products of plasma processing in N_2 gas were considered to be HCl, HF and F_2 for $CHClF_2$; HF and F_2 for CHF_3; and F_2 for CF_4. Such a conclusion was further supported by the fact that no significant amount of organic compounds was detected by infrared spectroscopy of the decomposition products. Regarding the carbon atoms of halide gases, it was considered that carbon might have been converted to some kind of tar found coated on the electrodes in the reactor. Further, in the plasma decomposition process of CF_4, no F scavenging reactions like that of CHF_3 and $CHClF_2$ decomposition occurred to form a

chemically stable hydrogen halide product. Hence, the F atoms derived from a CF_4 molecule were supposed to react with a CF_3 radical to form CF_4 again, and as a consequence, low decomposition ratios were achieved. Finally, to summarize this part, the higher decomposition ratios obtained for $CHClF_2$ were attributed to the low bond energy of C-Cl bond (342 kJ mol^{-1}) in contrast to those of C-H and C-F bonds.

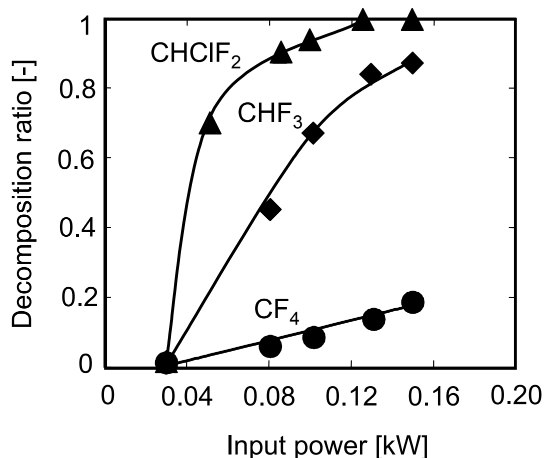

Figure 2. Decomposition of CF_4, CHF_3, and $CHClF_2$ under N_2 atmosphere

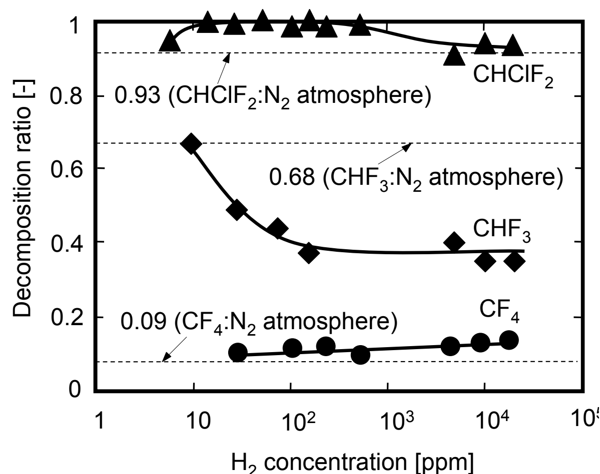

Figure 3. Effect of H_2 concentration on the decomposition of halide gases (CF_4, CHF_3, $CHClF_2$) in 0.10 kW

3.2. Effect of H_2 concentration on the decomposition of halides by non-thermal plasma

In the plasma decomposition of halide gases, the halogen atoms released by halide decomposition could be relatively easily converted to stable hydrogen halides, subsequently removable from the gas stream using an alkali absorbent. To achieve this goal, H_2 was introduced to the reactor and the effect of H_2 concentration on the decomposition of halides by non-thermal plasma was studied. Figure 3 shows the effect of H_2 concentration on the decomposition ratios of CF_4, CHF_3 and $CHClF_2$ at the fixed input power of 0.10 kW. In general, it can be seen that the decomposition ratio increased in order of $CHClF_2 > CHF_3 > CF_4$.

At first, regarding the decomposition of CF_4, higher decomposition ratios were obtained under H_2-N_2 atmosphere compared to decomposition ratio 0.09 obtained under N_2 atmosphere and the decomposition ratios slightly increased with an increase in H_2 concentration. It was considered that, under H_2-N_2 atmosphere, HF was formed by recombination of F and H atoms released by plasma decomposition of CF_4 and H_2, respectively. Then, as a consequence of HF formation, the recombination of CF_3 radical with F yielding the initial halide gas of CF_4 was assumed to be effectively hindered, which brought about higher decomposition ratios of CF_4 in the presence of H_2.

Further, in the case of CHF_3, the CHF_3 decomposition ratio was found to significantly drop when H_2 gas was added to N_2 atmosphere, and the decomposition ratio of only about 0.4 was obtained at H_2 concentration higher than 75 ppm. Decomposition of CHF_3 was expected to be initiated by a release of H atom of the C-H bond (410 kJ mol^{-1}) rather than by a dissociation of F atom from the C-F bond (472 kJ mol^{-1}). Thus, CHF_3 decomposition mechanism in the plasma reaction field was supposed to proceed via formation of H and CF_3 radicals. However, when the H_2 gas concentration in the plasma reaction field was increased, the free H atom was recombined with CF_3 radical to form back CHF_3, and consequently the decomposition of CHF_3 was significantly reduced.

Finally, the decomposition ratio of $CHClF_2$ increased with an increase in H_2 concentration and the decomposition ratio as high as 1.0 was achieved between 25 ppm and 510 ppm H_2. It was considered that the halogen atoms (Cl and F) were converted to HCl and HF in a hydrogen-enriched atmosphere, which brought about the promotion of decomposition. Although the decomposition of $CHClF_2$ can be hindered in the presence of free H atom as in the case of

CHF_3, it was assumed that the decomposition proceeded in H_2 atmosphere owing to the low bond energy of C-Cl bond.

Figure 4 shows a comparison of HCl and HF yields from the decomposition of $CHClF_2$ with and without 2 % H_2 in sample gas as a function of input power. It was found that the yields of HCl and HF increased with 2 % H_2 addition to gas stream, and HCl yield of 1.0 was obtained at the input power above 0.12 kW. Such a result indicated that the hydrogen in gas stream participated in halide decomposition reactions to form the final products of HCl and HF.

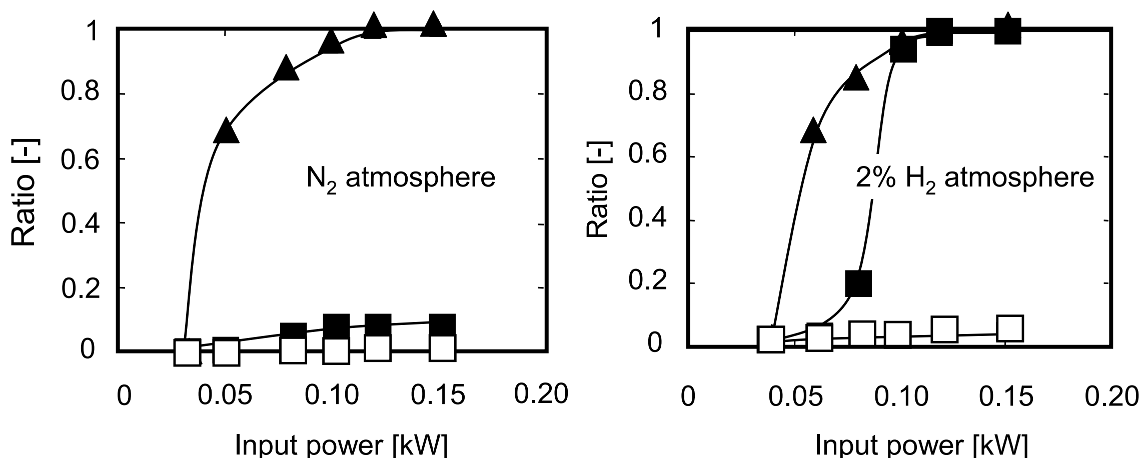

Figure 4. The yields of HCl and HF as a function of pulsed voltage in the decomposition of $CHClF_2$

▲: Decomposition ratio of $CHClF_2$, ■: Conversion of Cl to HCl, □: Conversion of F to HF

To summarize the results presented in Figures 3 and 4, it was considered that the presence of H_2 can result in either promotion or prevention of halide gases decomposition. At first, the promotion of the decomposition occurred when the halogen atoms released from halide gases preferentially reacted with free H atom to form stable hydrogen halides. As a consequence, the back formation of an initial halide gas was effectively hindered. By contrast, the prevention of the decomposition of halide gases is likely to take place for halide gases containing an H atom in their molecule. In such a case, the presence of free H atom in the plasma reaction field could lead to a shift in the reaction equilibrium towards the initial halide gas, since the decomposition of halide gases starts with the removal of H atom from a halide gas.

3.3. Non-thermal plasma decomposition of halide gases in O_2-N_2 atmosphere

In order to achieve oxidation of carbon present in halide gases to CO_2, the non-thermal plasma decomposition of halide gases was conducted at 0.12 kW under O_2-N_2 atmosphere, of which the O_2 concentration was adjusted to 0-20,000 ppm. Figure 5 shows the decomposition ratios obtained under O_2-N_2 atmosphere for CF_4, CHF_3 and $CHClF_2$. As seen in this figure, the decomposition ratio of CHF_3 decreased with an increase of O_2 concentration. The decomposition ratio of $CHClF_2$ as high as 1.0 was achieved in the O_2 concentration range of 25 ppm to 2,500 ppm. However, the decomposition ratio of $CHClF_2$ decreased when O_2 concentration was increased above 2,500 ppm. Finally, the decomposition of CF_4 did not take place in the whole O_2 concentration range used.

It was considered that, in the presence of O_2 in the gas stream, O radical was generated by a reaction of O_2 molecule with an electron, and consequently O_3 was formed by a reaction between O_2 and O radical. Then, as a result of these reactions, a significant portion of input energy was consumed for excitation and dissociation of O_2 molecules, which presumably led to a decrease in decomposition ratio of halide gases.

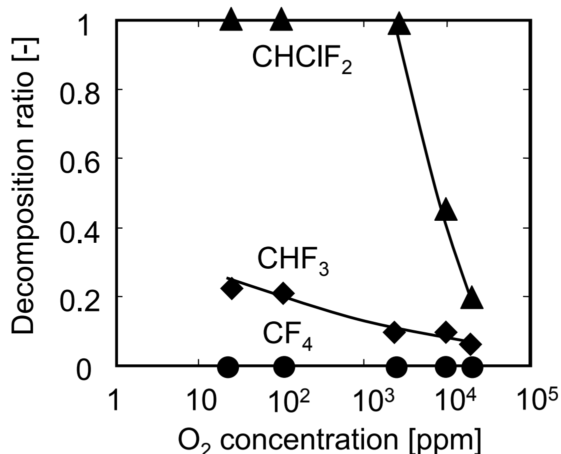

Figure 5. Effect of O_2 atmosphere on halide decomposition by non-thermal plasma

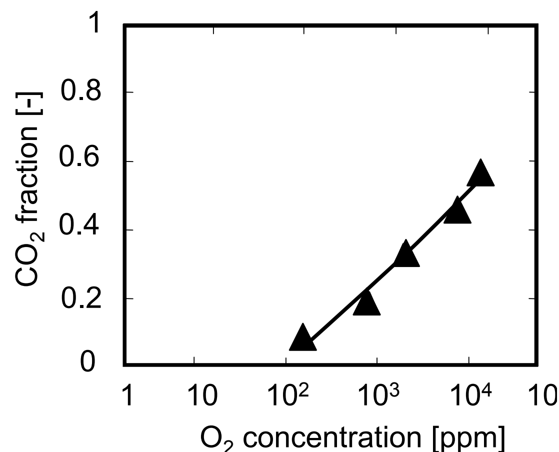

Figure 6. Effect of O_2 atmosphere on CO_2 formation in the decomposition halide gases

Furthermore, the reaction products of $CHClF_2$ decomposition under O_2-N_2 atmosphere were analyzed and the reaction products of COF_2, $COCl_2$ and desirable product of CO_2 were determined. Figure 6 shows the effect of O_2 concentration on the formation of CO_2 in non-thermal plasma decomposition of 100 ppm $CHClF_2$ at 0.12 kW. It can be seen that CO_2 fraction increased with an increase in O_2 concentration, which confirmed a positive effect of O_2 on the formation of CO_2.

4. CONCLUSIONS

The effects of H_2 and O_2 concentrations on the non-thermal plasma decomposition of CF_4, CHF_3 and $CHClF_2$ were investigated in this study. As a result, it was found that the decompositions of CF_4 and $CHClF_2$ were promoted by the presence of H_2. On the other hand, the decomposition ratio of CHF_3 decreased with an increase in H_2 concentration. As for the non-thermal plasma decomposition of halides under O_2-N_2 atmosphere, decomposition ratios of all halides employed were observed to decrease in the presence of O_2. However, the formation of desirable end-product of CO_2 significantly increased with an increase in O_2 concentration. Finally, it was showed that the decomposition of halide gases and the formation of reaction products can be controlled by changing the reaction conditions.

ACKNOWLEDGMENT

This research was supported by Grant-in-Aid for Scientific Research (B)(2) (No. 15310051) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

Kataoka, O. (2001) The present status of freon substitution (in Japanese), *Environmental Technology*, **30**(2), 93-96.

Mizuno K. (2001) Technology for Countermeasure of Destruction of Ozone layer (in Japanese), *Environmental Technology*, **30**(2), 87-88.

Oda T., Yamashita R., Takahashi T. and Masuda S., (1996) Atmospheric Pressure Discharge Plasma Decomposition for Gaseous Air Contaminants Trichlorotrifluoroethane and Trichloroethylene, *IEEE Trans. Ind. Appl.*, **32**(2), 227-232.

Sathiamoorthy G., Locke B.R., Finney W.C., Clark R.J. and Yamamoto T., (1999) Halon Destruction in a Gas Phase Pulsed Streamer Corona Reactor, *J. Adv. Oxid. Techol.*, **4**(4), 375-379.

Huang L., Nakajo K., Ozawa S. and Matsuda H., (2001) Decomposition of Dichloromethane in a Wire-in-tube Pulsed Corona Reactor, *Environ. Sci. Technol.*, **35**(6), 1276-1281.

Hari T. Nakajo K., Huang L., Kojima Y., Ozawa S. and Matsuda H., (2002) Influence of the Coexistence Gas and In-Situ Solid Absorbent on the Decomposition of Covalent Chlorides and Fluorides by Non-thermal Plasma, *Kagaku Kogaku Ronbunshu*, **28**, 522-527.