Influence of Coexisting Gases on Non-thermal Plasma Decomposition of Cl-and F-containing Halide Gases

Akira Yoko1, Takafuli Fujita1, Dalibor Kuchar1, Mitsuhiro Kubota1, Liwei Huang2, Hitoki Matsuda1

1. Department of energy Engineering and Science, Nagoya University, Nagoya, JAPAN
2. College of Biological and Environmental Engineering, Zhejiang University of Technology, Zhejiang, CHINA

Abstract: The present work is concerned with the destruction of halide gases containing Cl and F such as CF4, CHF3 and CHClF2 in a wire-in-tube pulsed corona reactor. In details, the influence of coexisting gases of H2 and O2 on non-thermal plasma (NTP) decomposition of CF4, CHF3 and CHClF2 was investigated. As a result, decomposition ratios of CF4 and CHClF2 by NTP were found to be higher under H2-N2 atmosphere than under N2 atmosphere. By contrast, the decomposition ratio of CHF3 under H2-N2 atmosphere was lower than that under N2 atmosphere. In the case of O2-N2 atmosphere, lower decomposition ratios of CF4, CHF3 and CHClF2 were obtained under O2-N2 atmosphere than under N2 atmosphere. Additionally, CHClF2 decomposition by NTP in the presence of O2 yielded the reaction products such as CCl2F2, COCl2 and CO2. Then, as the O2 concentration increased, the formation of undesirable product of CCl2F2 decreased, while the generation of CO2 increased.

Keywords: non-thermal plasma, halide gases, H2 concentration, O2 concentration

1. INTRODUCTION
Cl-and F-containing halide gases such as CF4, CHF3 and CHClF2 are widely used as organic solvents, refrigerants and dry etching agents in semiconductor production, air conditioning systems and other industrial processes. However, these gases are characterized by high Global Warming Potentials (GWPs), toxicity, and may remain in the atmosphere for a long period, due to their chemical stability [1, 2]. Hence, the effective techniques to prevent the release of halide gases into the environment are required.

In the recent years, non-thermal plasma (NTP) has been noted as one of the promising techniques for the decomposition of halide gases [3, 4]. In NTP decomposition, the decomposition of halide gases is divided into several steps such as initiation, propagation, and termination of radical reactions. In details, the dissociation and/or excitation of the targeted halide molecules by direct electron impacts, and the production of active reaction radicals and ions by electron dissociation and ionization of background gas molecules represent the initial step. Then, the subsequent chain reactions between the produced radicals and halide molecules propagate until stable products are formed.

The advantage of NTP process inheres in the possibility to decompose persistent halide gases, but some undesirable byproducts may be produced by the decomposition of halide gases under certain reaction conditions [3, 4]. Therefore, it is of great importance to prevent the production of secondary pollutants to achieve practical applications of NTP technology.

This study aims at preventing the production of toxic byproducts from the plasma decomposition of halide gases, and the effects of H2 and O2 on the decomposition behavior of CF4, CHF3 and CHClF2 were investigated. It was considered that, under H2-N2 atmosphere, the halogen atoms are converted to stable hydrogen halides. Meanwhile, under O2-N2 atmosphere, it was expected that carbon in the structure of halide gases is more liable to be converted to CO2 characterized by lower GWP than halide gases.

2. EXPERIMENTAL
A schematic diagram of the experimental system 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.

A prepared sample gas containing CF4, CHF3 or CHClF2 was introduced to the reactor at a fixed flow rate of 200 ml/min (residence time: 68 s) in all experiments. The concentrations of CF4, CHF3 and CHClF2 in all sample gas mixtures were adjusted to 25 ppm or 100 ppm under N2 gas, and H2 or O2 concentration in the sample gases were adjusted to 0-20,000 ppm. The sample gases before and after the plasma decomposition in the reactor were analyzed using an on-line FT-IR (SHIMADZU, FTIR-8700). In the FT-IR measurements, the concentrations of CF4, CHF3, CHClF2, HCl, and HF gases were analyzed five times and Cin, Cout, C1Cl, and C1HF represent the average values obtained.

The decomposition ratio of CF4, CHF3, and CHClF2 and the yield of HCl and/or HF from halide decomposition are defined by the following three equations:

\[
\text{Decomposition ratio of halides} = \frac{(C_{\text{in}}-C_{\text{out}})}{C_{\text{in}}} \quad (1)
\]
Yield of HCl = \( C_{\text{in}} - C_{\text{out}} \) / \( m \) \( \times \) \( n \) (2)

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

where \( C_{\text{in}} \) and \( C_{\text{out}} \) are the inlet concentration and the outlet concentration of the halide, \( m \) and \( n \) 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.

In addition, decomposition products such as CCl\(_4\), CHF\(_3\), and CO\(_2\) were analyzed by GC-MS (SHIMADZU, GC-17A), and CO\(_2\) fraction was defined as followed:

\[
\text{CO}_2 \text{ fraction} = \frac{C_{\text{CO}_2}}{C_{\text{in}} - C_{\text{out}}} (4)
\]

where \( C_{\text{CO}_2} \) is the concentration of CO\(_2\) in the decomposition products.

3. RESULTS AND DISCUSSION

3.1. Decomposition of halides by non-thermal plasma under \( \text{N}_2 \) atmosphere

Figure 2 shows the decomposition of three different halide gases (CF\(_4\), CHF\(_3\), and CHCIF\(_2\)) as a function of power input to the plasma reactor. The decomposition of halide gases was observed to start at an input power 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 CHCIF\(_2\) containing chlorine in the structure was found to be easier than decomposition of CF\(_4\) and CHF\(_3\), but CHCIF\(_2\) decomposition yielded undesirable byproduct of CCl\(_2\)F\(_2\). Finally, the decomposition of CF\(_4\) was found to be most difficult.

Under \( \text{N}_2 \) atmosphere, the plasma decomposition of halide compounds was initialized by dissociative electron attachment reactions generating Cl, F and H atoms and followed by a chain of radical reactions to form the final products.

Therefore, the production of CCl\(_2\)F\(_2\) in the case of CHCIF\(_2\) decomposition was attributed to the recombination of Cl atoms, dissociated by electron collision, with CCIF\(_2\) radicals.

Regarding the differences in decomposition ratios, the bond energies were assumed to play an important role. At first, the highest decomposition ratio obtained for CHCIF\(_2\) was attributed to the low bond energy of C-Cl bond in contrast to those of C-H and C-F bonds. Next, the products of HCl and HF, once formed by halide decomposition, presumably did not participate in further reactions because of 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\(_2\). Hence, the final products of plasma treatment in \( \text{N}_2 \) gas were considered to be HCl, HF and F\(_2\) for CHCIF\(_2\); HCl 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, except a slight amount of CCl\(_2\)F\(_2\). Regarding the carbon atoms of halide gases, it was considered that carbon might have been converted to some kind of tar found on the inner wall of a glass tube. Further, in the plasma decomposition process of CF\(_4\), F scavenging reactions yielding chemically stable hydrogen halide could hardly occurred since CF\(_4\) did not contain H in its structure. Hence, the F atoms derived from a CF\(_4\) molecule were supposed to react with a CF\(_4\) radical to form CF\(_3\), and as a consequence, low decomposition ratios were achieved.

![Figure 1: Experimental apparatus.](image)

**Figure 1:** Experimental apparatus.

**Figure 2:** Decomposition of halide gases under \( \text{N}_2 \) atmosphere (CF\(_4\), CHF\(_3\), and CHCIF\(_2\): 25ppm)

**Figure 3:** 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 alkaline absorbent. In accordance with such an assumption, 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 CHCIF\(_2\) at the fixed input power of 0.10 kW. In general, it can be seen that the decomposition ratio increased in order of CHCIF\(_2\) > CHF\(_3\) > CF\(_4\).
For the decomposition of CF₄, higher decomposition ratios were obtained under H₂-N₂ atmosphere compared to decomposition ratio of 0.09 obtained under N₂ atmosphere and the decomposition ratios slightly increased with an increase in H₂ concentration. It was considered that, under H₂-N₂ atmosphere, HF was formed by recombination of F and H atoms released by plasma decomposition of CF₄ and H₂, respectively. Then, as a consequence of HF formation, the recombination of CF₃ radical with F yielding the initial halide gas of CF₃ was assumed to be effectively hindered, which brought about higher decomposition ratios of CF₄ in the presence of H₂.

In the case of CHF₃, the CHF₃ decomposition ratio was found to significantly drop when H₂ gas was added to N₂ atmosphere, and the decomposition ratio of only about 0.4 was obtained at H₂ concentration higher than 75 ppm. Decomposition of CHF₃ was expected to be initiated by a release of H atom of the C-H bond rather than by a dissociation of F atom from the C-F bond. Thus, CHF₃ decomposition mechanism in the plasma reaction field was supposed to proceed via formation of H and CF₃ radicals. However, when the H₂ gas concentration in the plasma reaction field was increased, the free H atom was recombined with CF₃ radical to form back CHF₃, and consequently the decomposition of CHF₃ was significantly reduced.

Finally, the decomposition ratio of CHClF₂ increased with an increase in H₂ concentration and the decomposition ratio as high as 1.0 was achieved between 25 ppm and 510 ppm H₂. It was considered that the halogen atoms (Cl and F) were converted to HCl and HF in a hydrogen-enriched atmosphere, which led to the promotion of decomposition. Although the decomposition of CHClF₂ can be hindered in the presence of free H atom as in the case of CHF₃, it was assumed that the decomposition proceeded in H₂ 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 CHClF₂ with and without 2 % H₂ in sample gas as a function of input power. It was found that the yields of HCl and HF increased with 2 % H₂ 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.

3.3. Non-thermal plasma decomposition of halide gases in O₂-N₂ atmosphere

In order to achieve oxidation of carbon present in halide gases to CO₂, the non-thermal plasma decomposition of halide gases was conducted at 0.12 kW under O₂-N₂ atmosphere. In these experiments, O₂ concentration was varied in the range of 0 to 20,000 ppm. Figure 5 shows the decomposition ratios obtained under O₂-N₂ atmosphere for CF₄, CHF₃, CHClF₂, and CHF₂Cl. As seen in this figure, the decomposition ratio of CHF₃ decreased with an increase of O₂ concentration. The decomposition ratio of CHClF₂ as high as 1.0 was achieved within the O₂ concentration range of 25 ppm to 2,500 ppm. However, the decomposition ratio of CHClF₂ decreased when O₂ concentration exceeded a value of 2,500 ppm. Finally, the decomposition of CF₄ did not take place in the whole O₂...
It was considered that, in the presence of O₂ in the gas stream, O radical was generated by a reaction of O₂ molecule with an electron, and consequently O₃ was formed by a reaction between O₂ and O radical. Thus, a part of input energy was consumed for excitation and dissociation of O₂ molecules and O₃ formation, which resulted in insufficient energy input to achieve halide gas decomposition. As a consequence, decomposition ratio of halide gases decreased as O₂ concentration increased. Furthermore, the reaction products of CHClF₂ decomposition under O₂-N₂ atmosphere were analyzed and the reaction product of COCl₂ and desirable product of CO₂ were identified. Figure 6 shows the effect of O₂ concentration on the formation of CO₂ in non-thermal plasma decomposition of CHClF₂ at 0.08 kW. It can be seen that CO₂ fraction increased with an increase in O₂ concentration. In addition, the formation CCl₂F₂ was reduced as O₂ concentration increased, and no CCl₂F₂ was detected above O₂ concentration of 500 ppm. Such a result confirmed a positive effect of O₂ on the prevention of CCl₂F₂ formation as well as on CO₂ generation.

4. CONCLUSIONS
The effects of H₂ and O₂ concentrations on the non-thermal plasma decomposition of CF₄, CHF₃, and CHClF₂ were investigated in this study. As a result, it was found that the decompositions of CF₄ and CHClF₂ were promoted in the presence of H₂. By contrast, the decomposition ratio of CHF₃ decreased with an increase in H₂ concentration. As for the non-thermal plasma decomposition of halides under O₂-N₂ atmosphere, decomposition ratios of all halides were observed to decrease in the presence of O₂. Nevertheless, a positive effect of O₂ presence on the prevention of CCl₂F₂ formation as well as CO₂ generation was observed. Finally, the results presented in this study showed that the decomposition of halide gases and the formation of reaction products can be controlled by changing the reaction atmosphere.

REFERENCES