Decomposition of HFC134a Using Arc Plasma

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Abstract— Decomposition of HFC134a using arc plasma was examined. Influence of parameters such as plasma power supply current, amounts of supplied air and water vapor on combustion of HFC134a was determined. A decomposition rate of 99.99 % was achieved under optimum conditions. Gases generated by incomplete combustion of HFC134a were analyzed with GC-MS. It was found that trifluoroethylene and pentafluoroethane were formed when the plasma power supply current was under 30 A and that pentafluoroethane was formed when the combustion was carried out without water supply.

Keywords— Freon, Decomposition, Arc plasma, HFC134a

I. INTRODUCTION

Although chlorofluorocarbons (CFCs) or Freons have been used in many fields, the production was phased out by the end of 1995 after the serious impact of CFCs on stratospheric ozone layer depletion was predicted [1] and discovered. The depletion has been decelerated by substitution of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) for CFCs. However, HCFCs still have chlorine atoms in their structures influencing the ozone layer and were added to the list of Control Substances in the Montreal Protocol.

On the other hand, HFC134a was developed as an alternative refrigerant for CFC12 and is now widely used in air conditioners for automobiles. HFC134a totally replaced CFC12 for the renewal since the mid-1990s. Finding the alternatives to HCFC22 is difficult in a single component formulation, and thus two or three HFCs are used as a blended formulation in which HFC134a is included. Due to the hydrogen atoms in its structure, HFC134a has a shorter lifetime than CFCs in the atmosphere and does not deplete the ozone layer because of the absence of chlorine atoms.

However, HFC134a still has a relatively higher radiative forcing, resulting in a large Global Warming Potential (GWP) of 1300. Hepatotoxicity by inhalation of HFCs containing HFC134a has been reported [2-5]. At the EU Council meeting held on 14 October 2004 [6], a qualified majority among the 25 participating nations reached a political agreement on the use of new refrigerants with GWP of 150 or less. This political requirement calls for the phase-out of HFC-134a in all new vehicle models beginning in 2011, and in all new cars by 2017, and replacement with alternatives having GWPs lower than 150.

At present, about 80 % of recovered fluorocarbons in Japan are HCFC22. This percentage will gradually decrease due to a stepwise reduction in production, and accordingly, the recovery of HFCs is expected to increase. Among the recovered HFCs, HFC134a will be a main component due to the discharge from automobile air conditioners and commercial/household refrigerators that contain HFC134a in blend refrigerants such as R407C. The decomposition of HFC134a may be more favorable than recycling since recovered HFC134a may not compete with newly manufactured virgin HFC134a at market price.

Recovered fluorocarbons have been decomposed by several methods, such as combustion, cement kiln, plasma [7-10], and catalyst processes [11, 12]. However, these existing technologies are applied mainly in large scale facilities. To our knowledge, there is almost no report on decomposition technologies for a smaller amount of waste fluorocarbons. The authors have studied decomposition using arc plasma method suitable for on-site decomposition of waste fluorocarbons which were collected from air-conditioners. The power supply unit used in arc plasma has recently been miniaturized, bringing together high durability and a low cost. The simple control of plasma is an additional benefit. The authors have reported in a previous paper the first compact fluorocarbon decomposition device based on the arc plasma technology by which a decomposition rate of 99.99 % was attained. In this paper, we have extended our research into HFC134a that will be recovered in large quantities over the next years. The influence of various factors, such as plasma energy, air and water vapor supplies on the decomposition of HFC-134a, was studied on the same device. The emitted gases were analyzed by gas chromatography-mass spectrometry (GC-MS) to understand the decomposition process and to ensure safety of the equipment.

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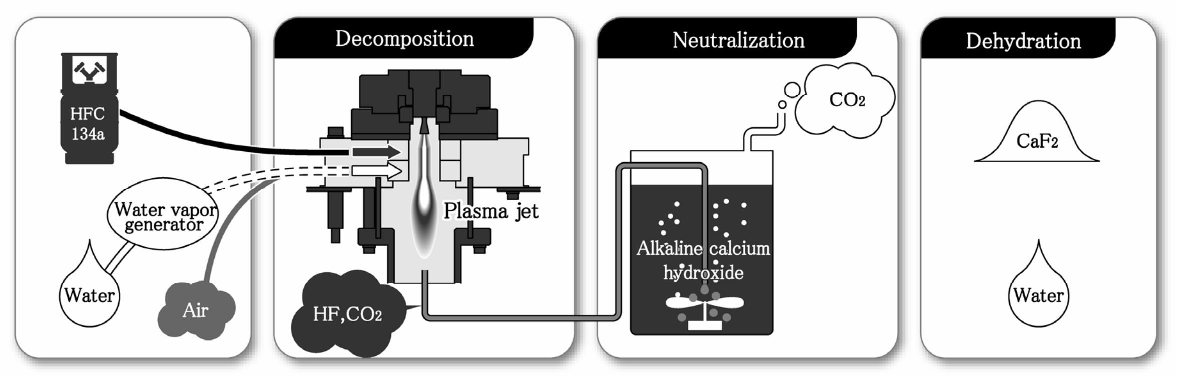

Fig. 1 Flowchart for HFC134a decomposition.

II. EXPERIMENTAL SETUP

A. Apparatus

The apparatus used in the decomposition experiment is described in a three stages flowchart (Fig. 1): decomposition by the torch, the neutralization, and the waste treatment by dehydration. The arc plasma torch was composed of electrodes and a gas inlet pipe. A cross-section diagram of the torch (diameter 150 mm, length 200 mm) is shown in Fig. 2. The electrodes were composed of an anode copper nozzle and a copper cathode. The cathode was equipped with a round hafnium chip at the center to protect it from high temperatures. Nitrogen, as a plasma gas, was introduced into the space between the electrodes. DC power was supplied to the electrodes, and cooling water was circulated into the blocks surrounding each electrode. A mixture of fluorocarbons, water vapor, and air was fed into the pyrolysis chamber near its roof where the nitrogen plasma, at around 2000 °C, flew in through the electrodes. Fluorocarbons were pyrolyzed inside the chamber and the effluent gas formed was transported to the neutralization equipment through a stainless tube. The DC power source from a plasma cutting-machine (Panasonic PF80) with a maximum output current of 80 A was used as the power source. The output current was measured by using a DC clump current meter (HIOKI E. E. Co. 3285).

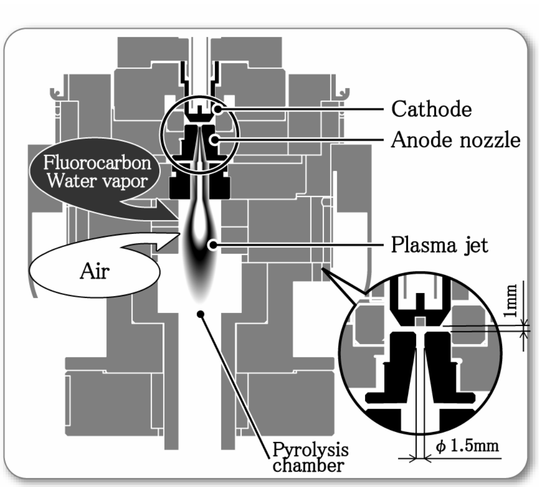

Fig. 2. Cross-section diagram of the torch.

The neutralization vessel was made of fiber-reinforced plastics (FRP) containing an aqueous solution of calcium oxide (Kawai-lime Co. not less than 72.5 % purity), which neutralized hydrogen fluoride generated in the decomposition reactions, as exemplified in Eq. (1). The calcium fluoride which formed was dehydrated in the waste treatment stage.

$$2\mathrm{HF} + \mathrm{Ca(OH)}_2 \rightarrow \mathrm{CaF}_2 + 2\mathrm{H}_2\mathrm{O} \qquad (1)$$

The target value of HFC decomposition rate was set at 99.99 % according to the guideline issued by Ministry of the Environment, and the experiments were conducted to achieve this target under the optimized conditions.

B. General method for gas analysis

The gases produced and unreacted fluorocarbons in the down stream were analyzed by a GC-MS (SHIMADZU Co. QP-5050) equipped with a capillary column (DB-624: 1.4 μm φ 0.25 mm x 60 m). The carbon monoxide was measured using an infrared (IR) gas concentration analyzer (Shimadzu CGT-7000). Fluorocarbon decomposition rates were calculated by the following equation:

$$\text{Decomposition rate (\%)} = \left(1 - \frac{\text{fluorocarbon in effluent gas}}{\text{total fluorocarbon fed}}\right) \times 100$$

C. Optimization of HFC134a decomposition

Experiments were carried out to optimize the decomposition of HFC134a in a system described in Fig. 1. In spite of stoichiometric reaction Eq. (2), excess water and oxygen were kinetically necessary to attain the complete decomposition rate, reaching 99.99 % conversion. Therefore, the experiments were conducted on the effects of supplies of plasma energy, water vapor, and air on the decomposition rate of HFC134a and the minimization of carbon monoxide formation.

$$CF_3CFH_2 + H_2O + \frac{3}{2}O_2 \rightarrow 4HF + 2CO_2 \qquad (2)$$

The HFC134a used in this experiment had a purity of 99.5 % or more (Asahi Glass Co. Ltd.). Water vapor was generated from highly purified water (Organo Co. G-10C).

a) Effects of plasma energy

There are two main factors to control the size of the plasma jet. One is the current, supplied from a DC power source, and the other is the plasma gas flow. In the present paper, we have studied the effect of DC current on the decomposition of HFC134a under the constant plasma gas flow (12 L/min), which was determined as a minimal requirement to form the stable plasma from economical and environmental points of view.

The HFC134a feed rate in the experiments was set at 2 kg/h based on the practical treating.

b) Effects of water vapor and air

According to Eq. (2), the stoichiometry of water vapor and oxygen required for decomposing HFC134a is:

HFC134a : water vapor : oxygen = 1 : 1 : 1.5 .

The mixing ratio of HFC134a, water vapor, and air was widely varied from the above stoichiometry. Examined ranges for water and air were 0.8 to 3 times and 0.8 to 1.8 times of the theoretically required amounts against HFC134a, respectively. The feed rate of HFC134a in this experiment was set at 2 kg/h, and the current output of the DC power source was set at the best value, 50 A, based on the results of Fig. 5.

D. Analysis of incomplete combustion exhaust

In order to examine the influence of plasma energy as well as the mixing ratio of water vapor and air, the gases generated in the decomposition of HFC134a under various conditions were collected in a Tedlar Bag (1 L) for GC-MS analysis.

a) Effects of plasma energy

When the current output of the DC power source was lowered below 30 A (determined in C.a), the decomposition rate decreased, leaving unreacted HFC134a. To study this condition, the current output of the DC power source was set at 20 A. The flow rate of HFC134a was set at 2 kg/h as described in C.a. The gases generated under these conditions were analyzed by GC-MS.

b) Effects of water vapor and air

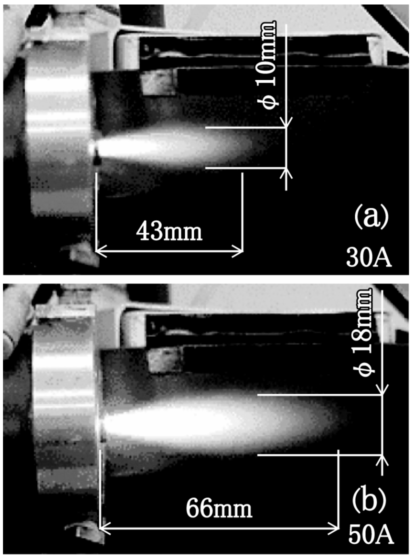

Fig. 3. Plasma jet at (a) 30 A and (b) 50 A.

The HFC134a decomposition was strongly affected in the absence of water vapor and air. In order to understand the significance of water vapor, decomposition of HFC134a was carried out without supplying water vapor, and the generated gases were analyzed by GC-MS. Further, to study the influence of air, decomposition was done with a shortage of supplied air (60 L/min instead of 90 L/min), and the generated gases were analyzed as well.

III. RESULTS

A. Optimization of HFC134a decomposition

a) Effects of plasma energy

The appearance of the plasma in an open space is shown in Fig. 3. When the current output of the power source increased, the light emitting from the plasma jet enlarged, and the heat in the pyrolysis chamber increased.

The correlation between voltage and current on the plasma torch is shown in Fig. 4. The decrease in voltage

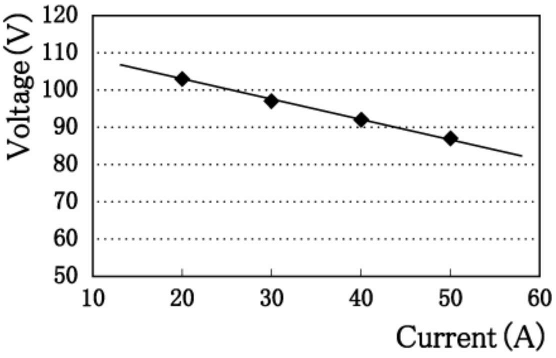

Fig. 4. Voltage / Current correlation.

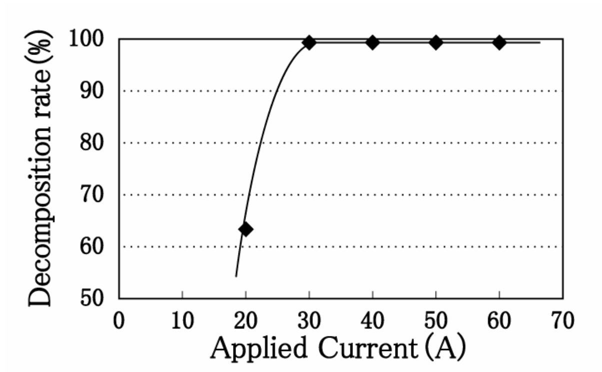

Fig. 5. Decomposition rate versus applied current.

with increasing current is a phenomenon generally seen in the arc plasma. Fig. 5 shows the decomposition rate as a function of the applied current. When the current was above 30 A, a decomposition rate of 99.99 % was achieved.

b) Effects of the water vapor and air supply rate

Water vapor and air supply was optimized. The dependencies of water vapor feed rate on decomposition rate and carbon monoxide generation are shown in Fig. 6 and Fig. 7, respectively. The feed rate of air was set at a fixed value of 90 L/min.

Based on the results in Figs. 6 and 7, the optimum range of water vapor feed was determined in the range of 11-13 mL/min.

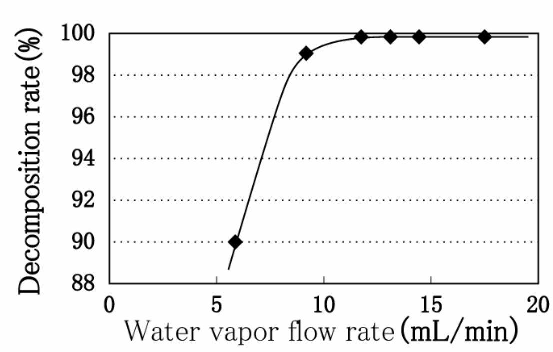

Fig. 6. Water vapor effect on HFC134a decomposition.

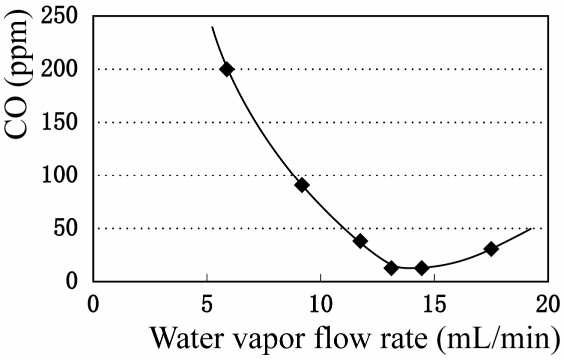

Fig. 7. Water vapor effect on CO generation.

The relationship between air feed and decomposition rate is shown in Fig. 8 while Fig. 9 shows the relationship between air feed rate and carbon monoxide generation. In these experiments (Figs. 8 and 9), the feed rate of water vapor was set at a fixed value of 12 mL/min. The results obtained in Figs. 8 and 9 indicate that the optimum flow range of air feed was determined between 80-90 L/min. It was concluded that both 99.99 % decomposition and a low emission level of CO (less than 100 mg/m^3 required for the United Nations Environment Program (UNEP) regulation) were attained under the optimum conditions.

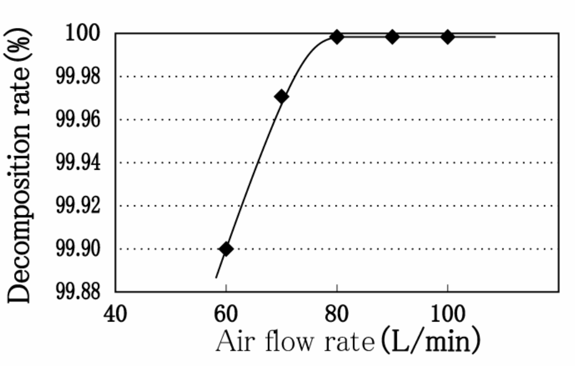

Fig. 8. Air flow effect on HFC134a decomposition.

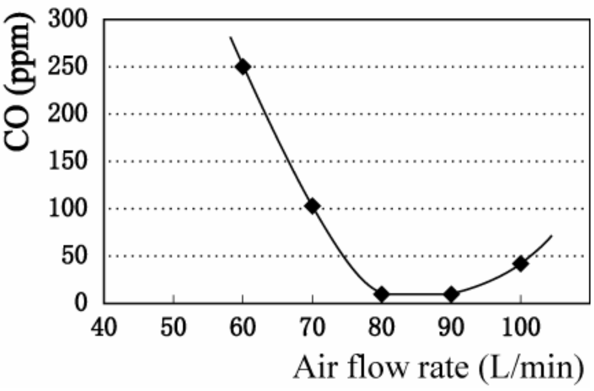

Fig. 9. Air flow effect on CO generation.

B. Analysis of incomplete combustion exhaust

a) Effect of plasma energy on combustion

Although the decomposition reaction proceeded normally without any formation of by-products under the optimum conditions with feeds of sufficient water and air, a small amount of by-products appeared under abnormal conditions. Fig. 10 shows gas chromatogram of the gas resulting from combustion of HFC134a under the deviated conditions (plasma power supplying 20 A). Seventy percent of the fed HFC134a (with a retention time of 4.8 min.) was decomposed and the unknown peak appeared at retention time of 4.63 min. Its mass spectrum is shown in Fig. 11 and was interpreted as a convolution

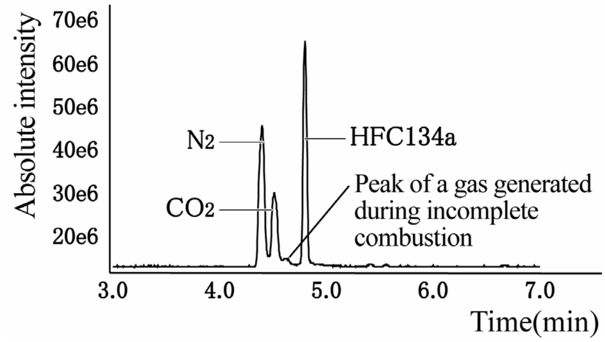

Fig. 10. Gas chromatogram of incomplete combustion exhaust at 20 A.

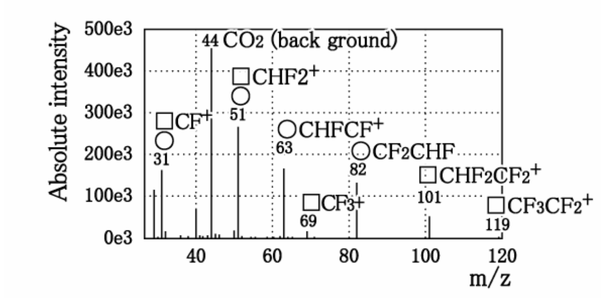

Fig. 11. Mass spectrum of incomplete combustion exhaust at 20 A (4.63 min).

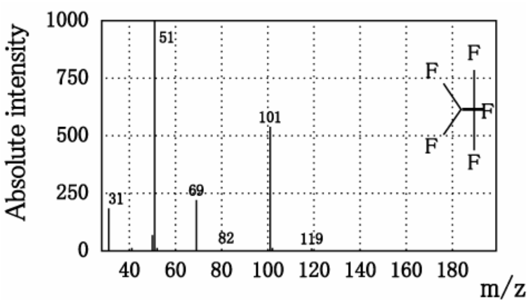

Fig. 12. Mass spectrum of CF2CHF (NIST).

of two species. The fragment ions marked by open circles were assigned to CF_2=CHF (by comparison with NIST data: Fig. 12).

The fragment ions marked by open squares were consistent with the mass spectrum of CF_3CF_2H (NIST data Fig. 13). The identification was further confirmed by the retention time (4.63 min) of a commercial CF_3CF_2H sample.

b) Effect of water vapor and air on combustion

The decomposition of HFC134a was carried out without water vapor feed at the HFC134a flow rate of 2 kg/h while keeping the air feed at 90 L/min. Eighty-five percent of the fed HFC134a was decomposed under these conditions. The gas chromatogram of the exhaust showed the peaks of the unknown and HFC134a at 4.6 and 4.8 min, respectively (Fig. 14). The mass spectrum of the unknown peak at 4.6 min coincided with the mass spectrum of CF_3CF_2H.

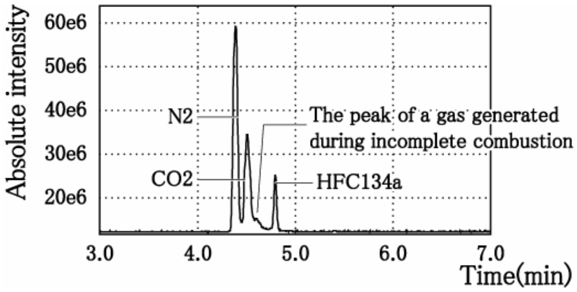

Fig. 13. Mass spectrum of CF3CF2H.

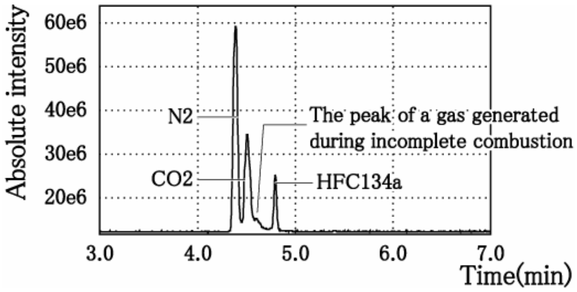

Fig. 14. Gas chromatogram of incomplete combustion exhaust.

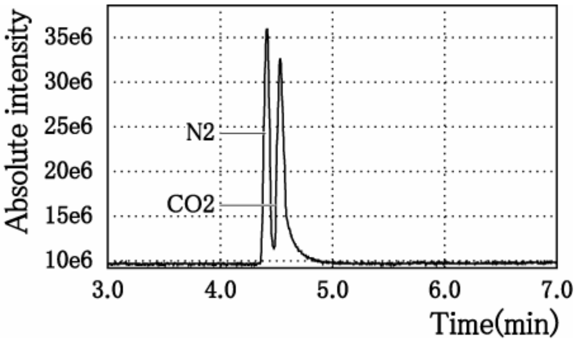

Fig. 13. Gas chromatogram of incomplete combustion exhaust under air deprived conditions (2/3 of optimum value).

In addition, the decomposition experiment was conducted with the air feed adjusted to 2/3 of the optimum amount while keeping the water vapor feed at 12 mL/min. The gas chromatogram of the exhaust is shown in Fig. 15. In this case, a 99.99 % decomposition rate of HFC134a was attained.

IV. DISCUSSION

As we have previously reported on the HCFC22 (CHF_2Cl) decomposition by the plasma reaction using a similar device, a current of 50 A from the plasma power supply was required to achieve a decomposition rate of 99.99 % [12]. In contrast, the results presented in this paper suggest that only 30 A was required for the decomposition of HFC134a at the same rate of 99.99 %.

HCFC22 has one hydrogen atom in the molecule, and

HFC134a has two hydrogen atoms. HCFC22 contains hydrogen with a ratio of 1 valence per 4 valences (25 %), and HFC134a contains hydrogen with a ratio of 2 valences per 6 valences (33 %). Although a simple comparison is difficult in a strict sense, it is considered that, due to higher hydrogen content in the molecule, HFC134a increases flammability, thus explaining the difference of optimum decomposition current from the power supply [13].

Takizawa et al. investigated the combustion of HFC41 (CH_3F), HFC152 (C_2H4F_2), and HFC161 (C_2H_5F), concluding that the combustion rate increased with the increase of hydrogen content in the molecules, thus the rate was in the order of HFC41, HFC152, and HFC161 [14]. Although the molecular structures reported here are not the same, our observation of the decomposition rates of HCFC22 and HFC134a are consistent with Takizawa's report.

Millward et al. examined the shock wave decomposition of HFC134a at 1170-1410 K and reported that eliminating hydrogen fluoride from HFC134a changes the main reaction as shown in Eq. (3) [15].

$$CF_3CFH_2 \rightarrow CF_2 = CHF + HF \quad (3)$$

We observed the generation of 1,1,2-trifluoroethylene in our experiment when the plasma power supply was lowered to 20 A from the optimal 50 A, suggesting that such conditions required for the HF elimination seems to be met in the rim of the plasma flame. In addition to 1,1,2-trifluoroethylene, a trace amount of pentafluoroethane (C_2HF_5) was also detected by GC-MS, but the formation mechanism (4) is not clear at the moment.

$$CF_3CFH_2 \xrightarrow[-H]{+F} CF_3CF_2H \quad (4)$$

The decomposition reaction was severely hindered under water-deficient conditions. Thus, a large amount of soot appeared by carbonation reaction and 15 % of HFC134a remained unchanged. Previous research proved that water molecules play an important role in the combustion reaction of the other fluorocarbons, such as CFC12 [16]. As seen in Eq. (2), carbon dioxide and hydrogen fluoride are the main products in the combustion of HFC134a. In general, water acts as a quencher for the combustion reaction. However, in this plasma condition, the water molecules serve both as a hydrogen source for HF formation and as an oxygen source for CO_2 formation during the decomposition of HFC134a.

Interestingly, C_2HF_5 was formed both under plasma energy supply shortage and water-deficient conditions, while 1,1,2-trifluoroethylene was formed only under the former plasma shortage conditions. The reason for the difference is under investigation.

V. CONCLUSION

With the aim of developing an on-site HFC gas decomposition device using arc plasma, the authors studied the optimization of HFC134a decomposition and the analysis of the gas generated during incomplete combustion.

By optimizing the output current of the plasma power supply, the supply rate of air and of water vapor, it was found that the proposed system can successfully achieve a HFC134a treatment rate of 2 kg/h (thus capable of treating a 20 kg cylinder per day) at a decomposition rate of 99.99 %.

It was found that the supply of 30 A to power the plasma was enough for 99.99 % decomposition of HFC134a, which is less than the 50 A necessary for the complete decomposition of R22. The increased hydrogen content in the molecular structure of HFC134a is thought to be responsible for the increased flammability of HFC134a.

It was determined that a small amount of by-products appeared by the incomplete combustion of HFC134a. Thus, CF_2=CHF and CF_3CF_2H were formed under power supply current shortage, and CF_3CF_2H was formed under the water-deprived condition.

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REFERENCES

[1] M. J. Molina, and F. S. Rowland, “Stratospheric sink for chlorofluoromethanes: chlorine atom-catalyzed destruction of ozone,” *Nature*, Vol.249, pp.810-812 , 1974

[2] T. K. Tromp, M. K. W. Ko, J. M. Rodriguez, N. D. Sze, “Potential accumulation of a CFC-replacement degradation product in seasonal wetlands,” *Nature*, Vol.376, pp327-330, 1995

[3] W. Tsai, “An overview of environmental hazards and exposure risk of hydro fluorocarbons (HFCs)” *Chemosphere*, Vol.61, Issue 11, pp1539-1547, 2005

[4] G. D. Ritchie, E. C. Kimmel, L. E. Bowen, J. E. Reboulet, J. Rossi, “Acute neurobehavioral effects in rats from exposure to HFC134a or CFC12”, *NeuroToxicology*, Vol.22, Issue 2, pp233-248, 2001

[5] P. Hoet, M. L. M Graf, M. Bourdi, *et al.*, “Epidemic of liver disease caused by hydro chlorofluorocarbons used as ozone-sparing substitutes of chlorofluorocarbons,” *The Lancet*, Vol.350, Issue 9077, pp556-559, 1997

[6] Press release 12908/04, (Press 283), of the 2610th EU Council Meeting, p11, 2004.

[7] M. Jasinski, J. Mizeraczyk, Z. Zakrzewski, “Decomposition of

freons in atmospheric-pressure air using coaxial-line-based low-power microwave torch plasma," *High Temperature Material Processes,* Vol.6, No.3, pp317-320, 2002

[8] J. D. Skalny, V. Sobek, P. Lukac, "Negative corona induced decomposition of CCl2F2," *NATO ASI Series*, G34A, pp151-365, 1993

[9] T. Oda, T. Takahashi, H. Nakano, and S. Masuda, "Decomposition of fluorocarbon gaseous contaminants by surface discharge-induced plasma chemical processing," *IEEE Trans. Ind. Applicat.,* Vol.29, pp787–792, 1993

[10] T. Oda, R. Yamashita, T. Takahashi, and S. Masuda, "Atmospheric pressure discharge plasma decomposition for gaseous air contaminants - Trichlorotrifluoroethane and Trichloroethylene," *IEEE Trans. Ind. Applicat.,* Vol.32, pp.227–232, 1996

[11] Y. Takita, T. Tanabe, M. Ito, M. Ogura, T. Muraya, S. Yasuda, H. Nishiguchi, T. Ishihara, "Decomposition of CH_2FCF_3 (134a) over metal phosphate catalysts," *Ind. Eng. Chem. Res.(Article)*, Vol.41, No.11, pp2585-2590, 2002

[12] M. Ohno, Y. Ozawa, A. Mizuno, T. Ono "Development of an on-site plasma-induced degradation device for Freon," *Research Institute of Environmental Technology,* Vol.36, No.6, pp427-433, 2007

[13] T. W. Dekleva, A. A. Lrndley, P. Powett, "Flammability and reactivity of select HFCs and mixtures," *ASHRAE Journal*, Vol.12, pp40-47, 1993

[14] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, "Burning velocity measurement of HFC-41, HFC-152, and HFC-161 by the spherical-vessel method," *Journal of Fluorine Chemistry*, Vol.127, pp1547-1553, 2006

[15] G. E. Millward, E. Tschuikow-Roux, "A kinetic analysis of the shockwave decomposition," *Journal Physic. Chem*, Vol.76, No.5, pp292-298, 1973

[16] K. Maeno, S. Udagawa, K. Toyada, "Decomposition experiment of hydro-fluorocarbon gas by pulsed TEA CO_2 laser," *International Symposium on Gas Flow, Chemical Lasers, and High-Power Lasers,* Vol.5777, pp1034-1039, 2004