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CFC Destruction by Steam Plasmas Generated by Atmospheric DC Discharge

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Abstract
Characteristics of 100%-steam plasma with DC discharge were investigated for the application of halogenated hydrocarbon decomposition. The presented steam plasma system is portable light-weight plasma generation system that does not require gas supply unit. The system has high-energy efficiency resulting from the unnecessity of water-cooling. The decomposition efficiency of 99.9% was obtained up to 0.43 mmol/kJ of the ratio of HFC-134a feed rate to the arc power.

1. Introduction

Halogenated hydrocarbons have been used widely as refrigerant, working fluid, foaming agent for plastics and insulating material, solvent, because of inflammability, no toxicity, and chemical stability. However, chlorofluorocarbons (CFCs) are revealed to be the matter of global warming and ozone depleting. Therefore, manufactures of CFCs have been prohibited by Montreal Protocol since 1987. Destruction of CFCs as well as research for the alternatives has been required.

CFCs can be effectively decomposed by reaction with hydrogen and oxygen; hydrogen combine with halogen to form halogenated hydrogen, oxygen combine with carbon to form CO and CO_2 to prevent reformation of by-products. Thus, destruction of CFCs with hydrogen and oxygen was demonstrated by argon plasmas [1]. However, hydrogen has disadvantage of high cost and explosibility, therefore steam plasmas that produce hydrogen and oxygen at high temperature are more favorable for industrial application of waste treatment. Radio frequency (RF) steam plasmas have performed high level destruction with ppm range concentration of destructed CFCs or halon in the exhaust gas [2]. Besides, small microwave steam plasmas for CFCs destruction have been used commercially [3].

Direct current (DC) plasma can be generated efficiently with simpler configuration than RF and microwave plasmas. Applications of DC argon plasma for CFCs destruction have already been operated with injection of oxidizing gas such as steam and oxygen [4-6]. DC steam plasma process was also applied to various waste treatments such as decomposition of PCB [7]. Nevertheless, the electrodes require protection from erosion derived from high reactivity of steam plasmas. In the PCB decomposition, tungsten cathode is protected by nitrogen or argon. In the steam plasma generation with several plasma gases, thoriated tungsten cathode is protected by using hydrogen [8].

Plasma generation system generally requires complex sub-equipments such as gas supply unit or cooling system. Especially steam plasma system requires sub-equipments such as heater to prevent condensation of steam through the reactor. Thus, efficient steam plasma generation system has been required for industrial application. The purpose of this paper is to generate stable steam plasma using portable light-weight DC plasma system without water-cooling and gas supply unit. Another purpose is to investigate decomposition mechanism of hydrofluoroethylene (HFC-134a) by the steam plasma.

2. Thermodynamic consideration

Thermodynamic equilibrium was calculated from the minimization of Gibbs free energy of the system with assumption that complete thermodynamic equilibrium is achieved. The chemical composition obtained from the calculation is probably not practical, however the thermodynamic equilibrium is useful to assess the important species in CFC decomposition. Thermodynamic equilibrium was calculated by FACT (Centre for Research in Computational Thermochemistry, Canada) to determine the species in plasma. FACT is database software for searching chemical equilibrium composition in which Gibbs free energy is the lowest.

Thermal equilibrium composition of pyrolised HFC-134a is shown in **Fig. 1**. CF_4 is the stable by-product under 2500 K, while HFC-134a does not exist. In the destruction of HFC-134a, suppresion of CF_4 production is strongly required, because the global warming potential (GWP) of CF_4 is 6500 times higher than that of CO_2. Chemical composition of water is shown in **Fig. 2** as function of temperature. H_2O dissociates to O and H at 3500 K. These dissociated O and H play important roles in the reformation control of undesirable

by-products.

Thermal equilibrium composition of HFC-134a decomposition with steam is presented in **Fig. 3**. The ratio of HFC-134a to steam is decided from the stoichiometric coefficient of following reaction.

$$C_2H_2F_4 + 4H_2O \rightarrow 4HF + 3H_2 + 2CO_2$$

Hydrofluorine is the most stable fluoride under 3800 K without undesirable by-products. Therefore, steam plasmas are suitable for decomposition of HFC-134a. HFC-134a with steam produces H_2 and CO from 800 K to 3500 K, resulting in reduction atmosphere.

Thermal equilibrium composition of HFC-134a decomposition is shown in **Fig. 4** in the case of low supply of steam:

$$C_2H_2F_4 + 2H_2O \rightarrow 4HF + H_2 + 2CO.$$

Hydrofluorine is the most stable fluoride under 4400 K without undesirable by-products.

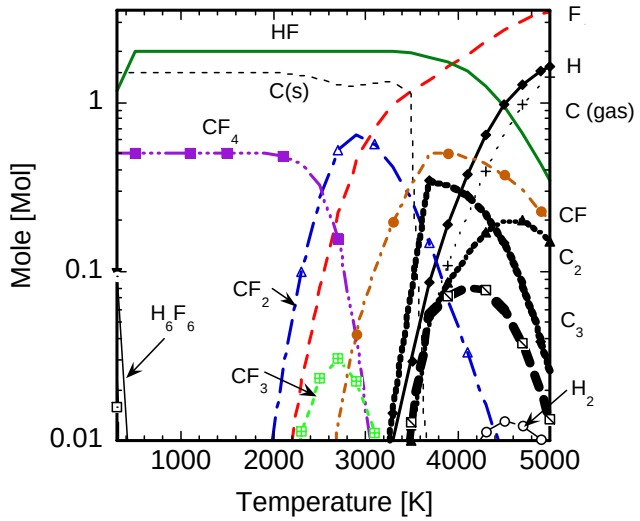

Fig. 1 Equilibrium composition of pyrolized HFC-134a.

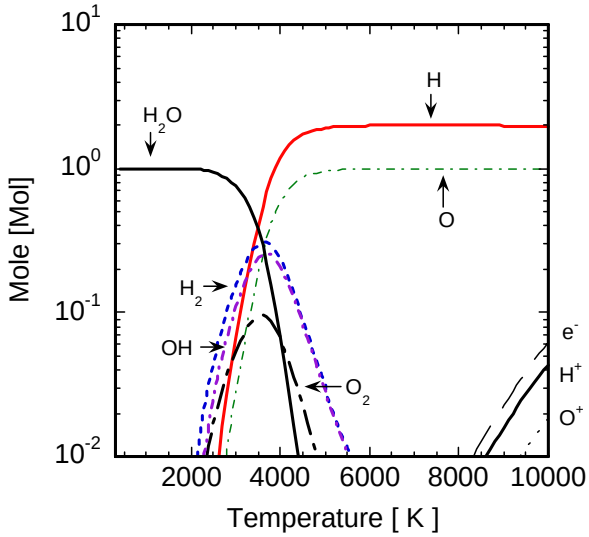

Fig. 2 Equilibrium composition of H_2O

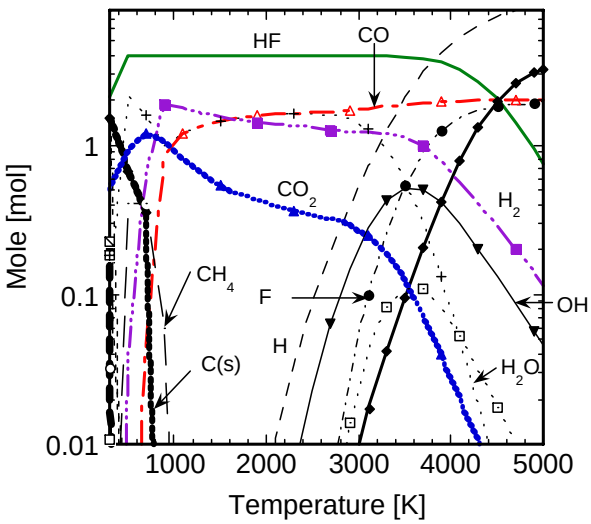

Fig. 3 Equilibrium composition of 20mol% HFC-134a and 80mol% steam.

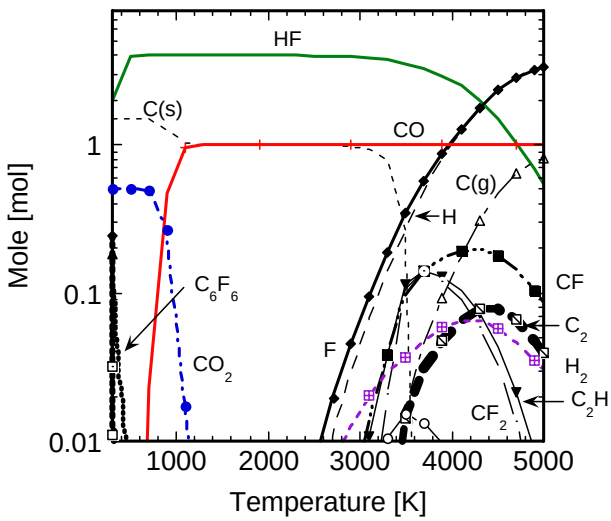

Fig. 4 Equilibrium composition of 33mol% HFC-134a and 67mol% steam.

3. Steam Plasma Generation

The steam plasma torch is a DC thermal plasma generator of coaxial design with a cathode of hafnium embedded into the copper rod and a nozzle-type copper anode. When steam plasmas are applied to waste treatment, the use of additional steam generator is unsuitable, because the steam generator requires larger and complicated system including the heating-up of the water feeding line preventing steam from condensation. The presented plasma torch can generate 100%-steam plasma without commercially available steam generator.

The configuration of the DC steam plasma torch is presented in **Fig. 5**. The advantage of the presented steam plasma torch is generation of 100%-steam plasma by DC discharge. The features of the torch result from the simple steam generation; water from the reservoir is heated up and evaporated at the anode region to form the plasma supporting gas. Simultaneously, anode is cooled by the water evaporation, therefore the electrodes do not require additional water-cooling. The distinctive steam generation method provides the portable light-weight plasma generation system that does not require the gas supply unit, as well as the high energy efficiency resulting from the unnecessity of the additional water-cooling.

The arc power was 0.65-1.47 kW with the arc current of 4.0-7.0 A. During the arc discharge, water feed rate is set at 325 mmol/min.

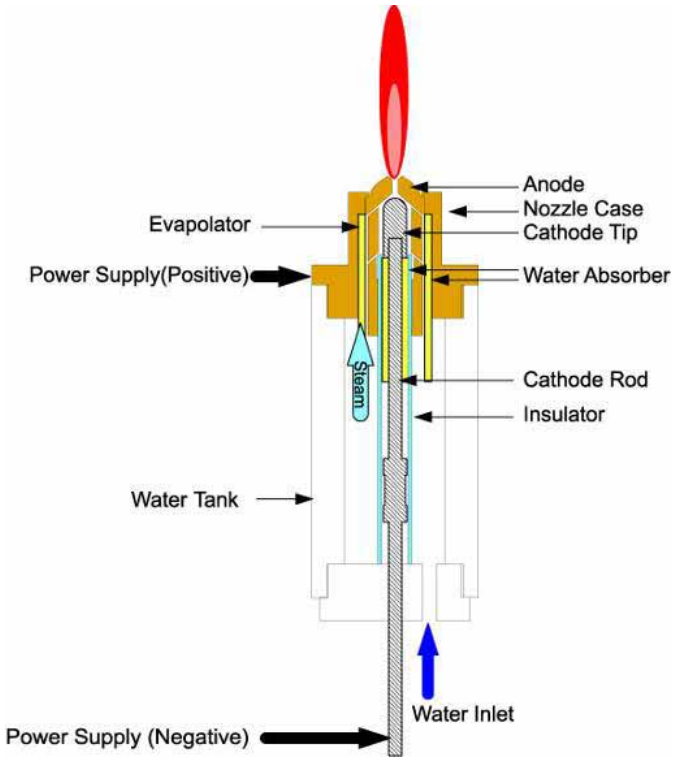

Fig. 5 Schematic diagram of steam plasma torch with DC discharge.

4. CFC Destruction System

Reaction tube and neutralization vessel are presented in **Fig. 6**. Reaction tube is water-cooled Inconel C-276 tube with inside diameter of 14 mm. Inconel C-276 is used as corrosion resistance material. HFC-134a was injected from the water-cooled tube at 8 mm upper from the nozzle exit of the steam plasma and at 7 mm outer from the center. Neutralization vessel is combined to the reaction tube to absorb F_2 and HF generated from the HFC-134a decomposition. Neutralization vessel is filled with pure-water monitored with pH meter. The destruction was performed with changing the feed rate of HFC-134a up to 185 mmol/min. The gas chromatography for monitoring of the exhaust gas indicated that productions of by-product such as CF_4 were not found. After the decomposition of HFC-134a, total organic compounds (TOC) and organic compound (OC) were measured to estimate the by-product concentration in the

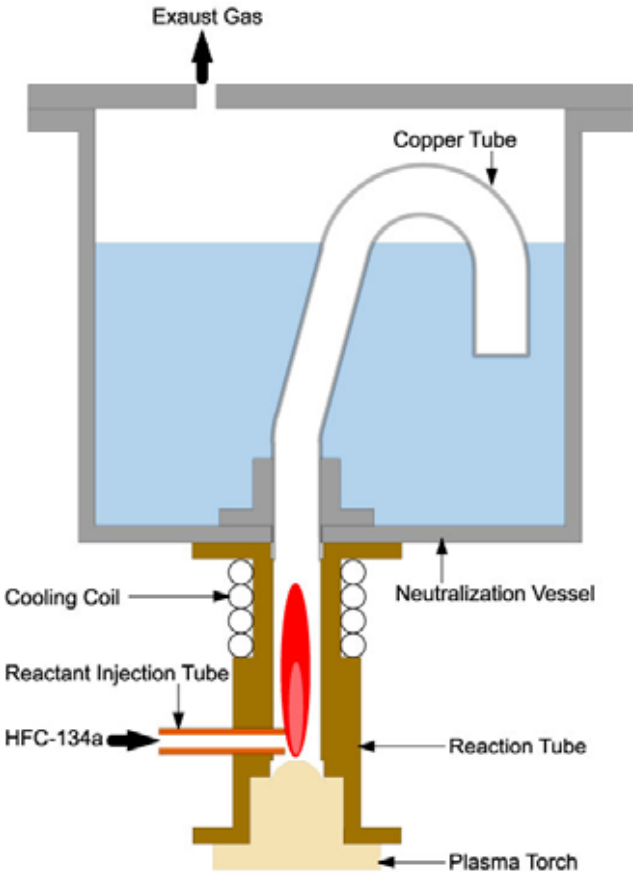

Fig. 6 Schematic diagram of CFC destruction system with steam plasma generator and neutralization vessel.

water with the pH measurements by neutralization titration.

5. CFC Decomposition Results

The decomposition efficiency of HFC-134a can be evaluated from the recovery of the fluorine which is produced from the decomposition. Fluorine in the decomposition gas easily dissolves in water, therefore the recovery of fluorine is a good indication of the HFC-134a decomposition. The exhaust gas composition also provides the decomposition efficiency, however the estimation of the decomposition efficiency is complicated owing to the unknown peaks of the gas chromatographs and to the calibration of all peaks.

The decomposition results of HFC-134a with different injection locations are presented in **Fig. 7**. The recovery of fluorine was estimated from the pH measurements by neutralization titration of the water for the exhaust gas treatment after the HFC-134a decomposition. The injection of HFC-134a at the 8 mm from the nozzle exit of the steam plasma gives the complete recovery of fluorine, indicating the complete decomposition of HFC-134a. More downstream injection of HFC-134a leads to a decrease in the recovery of fluorine, because the plasma temperature decreases with the distance form the nozzle exit.

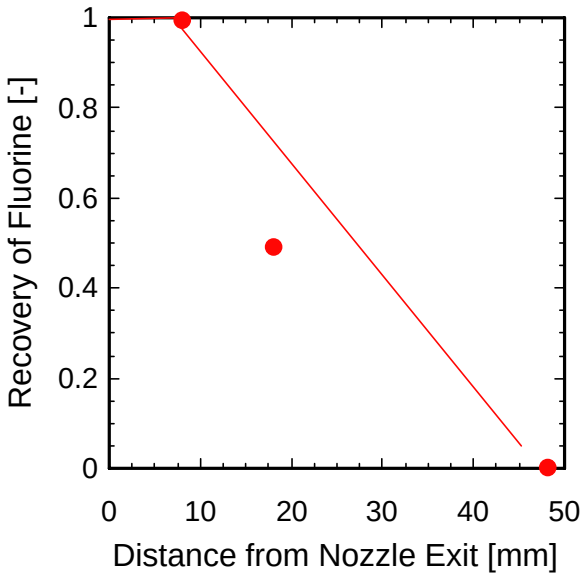

Fig. 7 Effect of HFC-134a injection location on recovery of fluorine. Arc power: 1.10 kW.

The effect of injection location of HFC-134a on the exhaust gas composition is shown in **Fig. 8**. HFC-134a injection at shorter distance from the nozzle exit leads to larger production of CO and CO_2. These results indicate the enhanced decomposition can be obtained from the HFC-134a injection at higher temperature. Besides, the selectivity of CO decreases with the distance, because the selectivity of CO decreases with a decrease in the decomposition temperature. This trend can be also expected from the equilibrium composition as shown in Figs. 3 and 4.

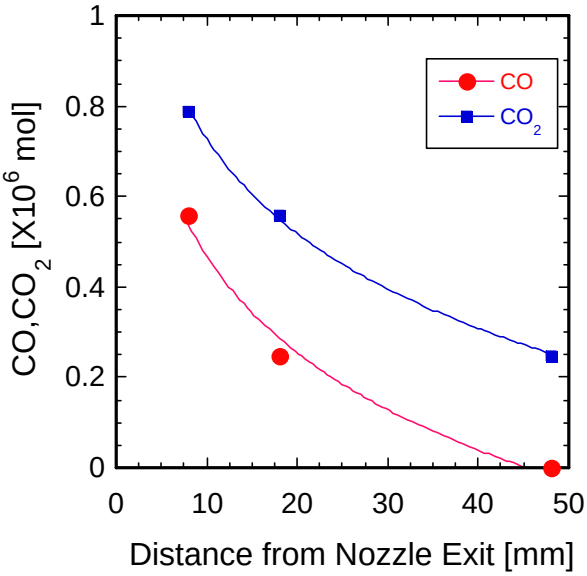

Fig. 8 Effect of HFC-134a injection location on CO and CO_2 production. Arc power: 1.10 kW.

The feed rate of HFC-134a into the high-temperature region has critical effect on the decomposition, because the maximum feed rate of HFC-134a depends on the enthalpy of the plasma. The effect of the feed rate on the recovery of fluorine is presented in **Fig. 9**. The recovery of fluorine at 99.9% can be obtained at 23 mmol/min of HFC-134a feed rate and at 1.47 kW of the arc power. The feed rate of HFC-134a over the threshold brings about the sudden decrease in the recovery of fluorine.

The effective decomposition is related to the feed rate of HFC-134a as well as the arc power, therefore the ratio of the feed rate to the arc power was calculated to estimate the decomposition efficiency. The effect of the ratio of the feed rate to the arc power on the recovery of fluorine is shown in **Fig. 10**, showing the comparable decomposition efficiency of the presented system with other CFC destruction systems. The recovery of fluorine with 99.9% can be obtained up to 0.43 mmol/kJ, hence the maximum feed rate is estimated to be 160 g/h at 1 kW of the arc power.

Effect of the feed rate of HFC-134a on CO_2 and CO production in the exhaust gas is shown in **Figs. 11** and **12**, respectively. Larger feed rate of HFC-134a leads to decreasing of CO_2 and CO production. This is

due to the temperature decrease owing to the larger feed rate of HFC-134a and to the insufficient mixing of HFC-134a at the high-temperature region of the steam plasma. Moreover, larger amount of CO is produced at higher arc power, resulting from the enhanced decomposition.

Fig. 13 presents the effect of feed rate of HFC-134a on the selectivity of CO in the exhaust gas. The selectivity of CO decreases with increasing of the feed rate of HFC-134a and with decreasing of the arc power, because CO is more stable than CO_2 at higher temperature. The temperature decrease in the plasma resulting from larger feed rate of HFC-134a is predictable from Fig. 13.

Analysis of by-product from the HFC-134a decomposition is presented in **Fig. 14**. Total organic carbon (TOC) in the water for the exhaust gas treatment was measured after the decomposition. There is a tendency of a decrease in TOC with increasing of the feed rate of HFC-134a, but the TOC can be negligible compared with the solubility of HFC-134a in water (1.5×10^{-2} mol/L). The measured organic carbon (OC), which is not shown, is also negligible in the water. Therefore, the main component in the water is HF after the HFC-134a decomposition.

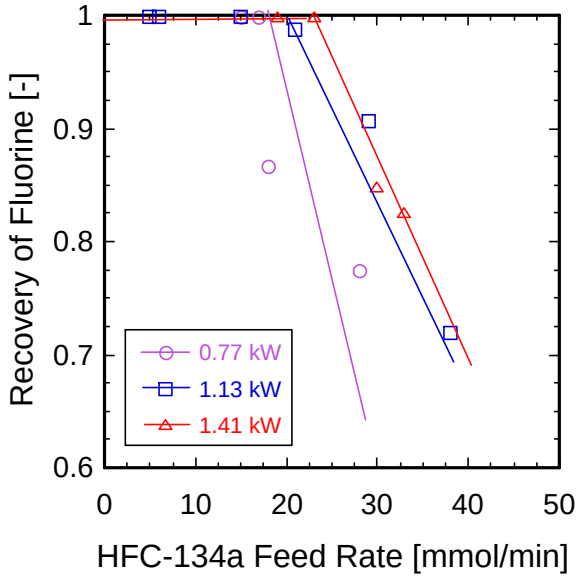

Fig. 9 Effect of HFC-134a feed rate on recovery of fluorine.

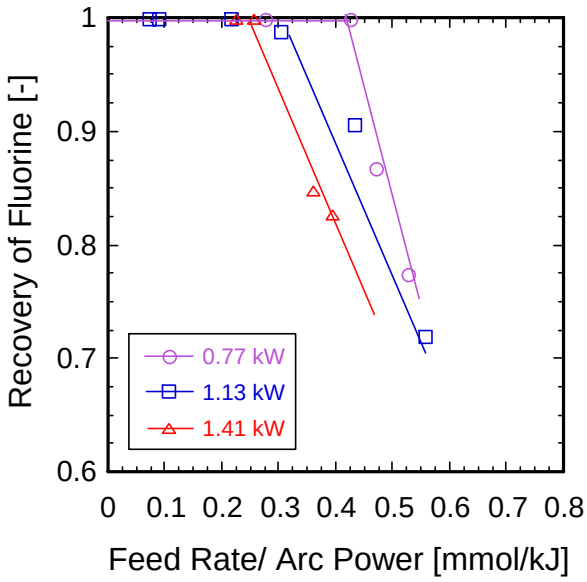

Fig. 10 Recovery of fluorine as a function of the feed rate normalized to the arc power.

6. Conclusions

Stable DC 100%-steam plasma generation under atmospheric pressure was developed for CFC decomposition.

Decomposition of HFC-134a produces CO, CO_2, and H_2 in the exhaust gas, and HF which can be recovered in the water of the neutralization vessel. The total organic carbon as the by-products after the decomposition can be negligible in the water. The decomposition efficiency of 99.9% can be obtained up to 0.43 mmol/kJ of the ratio of HFC-134a feed rate to the arc power, hence the maximum feed rate is estimated to be 160 g/h at 1 kW of the arc power. More detailed investigation is required to optimize the plasma system for industrial application.

Thermal plasmas such as steam would provide more capability for waste treatments, if thermal plasmas are utilized effectively as chemically reactive gas. Application of plasma systems for waste treatment is expected to downsize the system, reduce hazardous substances in exhaust gas, finally low cost of waste treatment.

4. References

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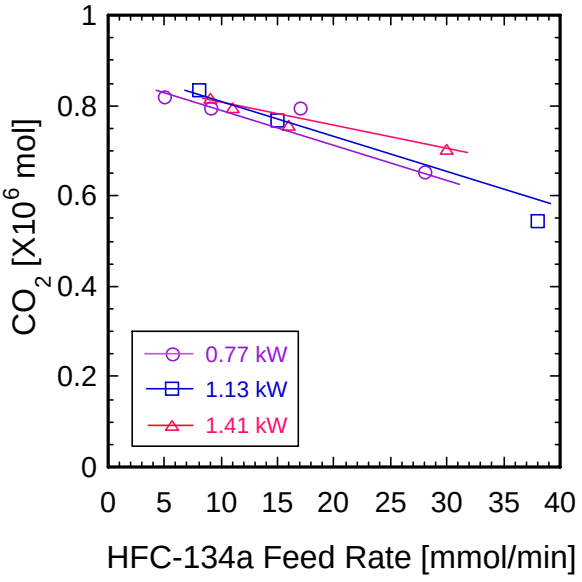

Fig. 11 Effect of f HFC-134a feed rate on CO_2 production in exhaust gas.

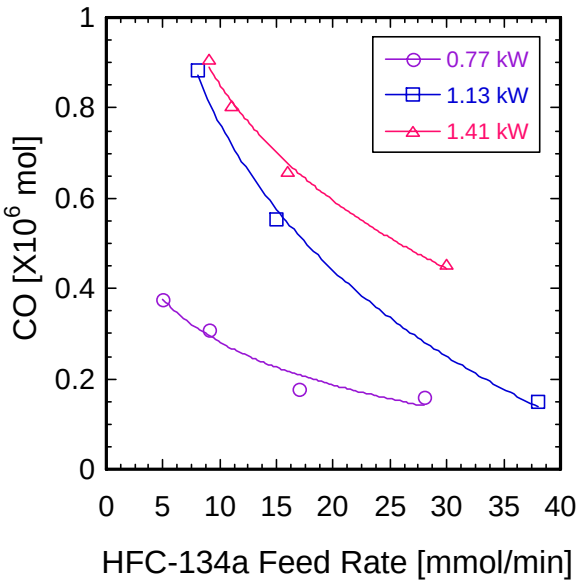

Fig. 12 Effect of HFC-134a feed rate on CO production in exhaust gas.

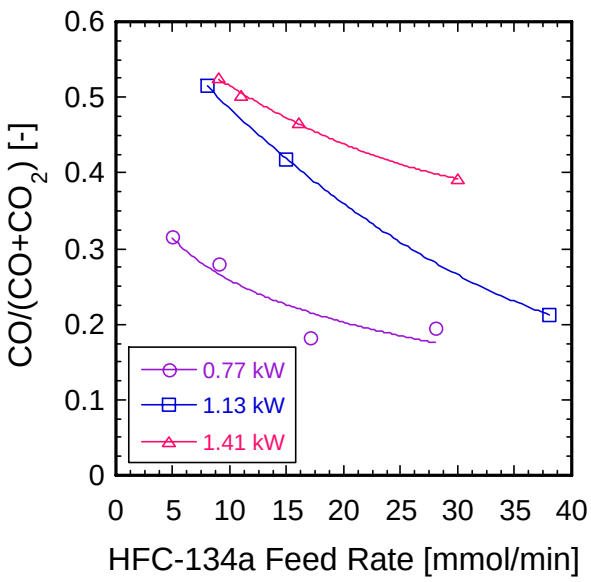

Fig. 13 Effect of HFC-134a feed rate on selectivity of CO in exhaust gas.

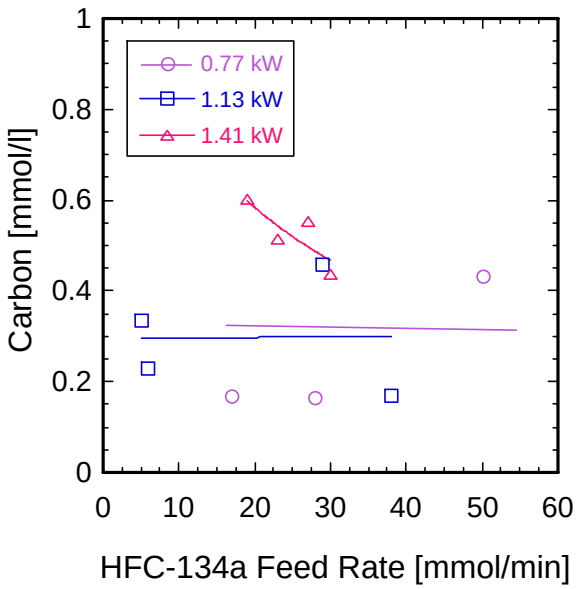

Fig. 14 Total organic carbon in water of neutralization vessel after decomposition.