

## Development of Technologies for Recovery and Removal of Fluorinated Compounds Causing Global Warming ( Abstract of the Report )

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### 1. Introduction

According to the rationale of the Montreal Protocol, HCFCs, substitutes for CFCs, have been rapidly replaced by HFCs and PFCs, whose ozone depletion potentials are zero. Due to this shift, HFC emission in FY 1997 greatly increased by 18.4 % compared to FY 1996. On the other hand, use of HFCs, PFCs, and SF<sub>6</sub> causes global warming since their global warming potentials are far larger than that of CO<sub>2</sub> and their lifetimes are much longer. The reduction and phase-out of the above fluorinated compounds is the global issue. However, effective systems have not been constructed for recovery and removal of these fluorinated compounds due to a variety of their chemical structures, depending on uses such as foaming, etching semi-conductors, electrical insulation, etc.

The goals of this research consist in the development and complementary systemization of the recovery technologies in use of highly efficient separation membranes and hydrates, and removal technology based on nonthermal plasma. This kind of technological hybridization, which is indispensable in constructing systems for recovery and removal of HFCs, PFCs, and SF<sub>6</sub>, eventually contributes to the suppression of their dispersion to the atmosphere from a variety of emission sources, resulting in the prevention of global warming.

### 2. Research Objective

This research aims at preventing the dispersion of fluorinated global warming compounds by cooperatively conducting the following three studies.

- (1) Development of the separation process with membranes for recovery of fluorinated global warming compounds
- (2) Development of the process for recovery and regeneration of fluorinated global warming compounds with hydrates

- (3) Development of the technology decomposing fluorinated global warming compounds with nonthermal plasma

### 3. Research Method

- (1) Development of the separation process with membranes for recovery of fluorinated global warming compounds

Novel membranes for recovery of PFCs and SF<sub>6</sub>, which are utilized in semi-conductors manufactures, were fabricated from glassy polymers and carbons. The structures of these membranes were analyzed and modified to improve their separation performances for PFCs and SF<sub>6</sub> in N<sub>2</sub>. A small-scale membrane module was finally fabricated and evaluated for a feasibility study.

Mathematical equations for back diffusion mixing caused by a rapid increase of PFCs concentration along the module axis were formulated and analyzed to design a high performance membrane module for PFCs recovery from a diluted stream (PFCs<1%).

Analyses of process simulation were also carried out for the case of SF<sub>6</sub> recovery from a source containing 1% SF<sub>6</sub> with membranes followed by a gas-liquid separator operated at 15 .

- (2) Development of the process for recovery and regeneration of fluorinated global warming compounds with hydrates

A new separation method using gas hydrate formation is proposed for separating HFC-134a from gas mixtures containing N<sub>2</sub> and HFC-134a. The feasibility of this separation method was investigated from various points of view. First, to determine the mixed hydrate stability region, three-phase equilibria of hydrate (H), liquid water (LW), and vapor (V) for HFC-134a + N<sub>2</sub> + water mixtures with various HFC-134a vapor compositions were closely examined in the temperature and pressure ranges of 275-285 K and 0.1-2.7 MPa, respectively. Second, the compositions of the hydrate and vapor phases at a three-phase equilibrium state were analyzed for the identical mixtures at 278.15 and 282.15 K to confirm the actual separation efficiency. Third, kinetic experiments were performed to monitor the composition change behavior of the vapor phase and to determine the time required for an equilibrium state to be reached.

- (3) Development of the technology decomposing fluorinated global warming compounds with nonthermal plasma

Reactivities of HFC-32, HFC-23, HFC-134a, HFC-125, and PFC-14 in nonthermal plasma were investigated with ferroelectric packed-bed (**FPR**), silent discharge (**SDR**), surface discharge (**SFR**), and pulsed corona (**PCR**) reactors and catalysts such as MnO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub>, and AlPO<sub>4</sub>. Reactor power consumptions were measured with a high-voltage

amplifier, a function generator, and an oscilloscope. AC frequency varied in the range of 50Hz to 20kHz. Applied voltage was increased up to 16kV. Substrate concentration, background gas composition, and gas flow rate were adjusted with sets of mass flow controllers and a gas mixer. Byproduct identification and determination of substrate conversions and byproduct yields were carried out by FTIR with a BaF<sub>2</sub> window plate and a 10 cm gas cell.

#### 4. Results and Discussion

##### (1) Development of the separation process with membranes for recovery of fluorinated global warming compounds

From the results of screening experiments, 6FDA-BAAF polyimide was selected as a candidate of membrane material for PFCs separation. Hollow-fiber membranes were spun from 6FDA-BAAF by the techniques of solvent-casting and phase inversion. The hollow-fiber membrane exhibited higher permeation fluxes for N<sub>2</sub> than those of commercially available membranes. However, ideal separation factors (ISF) of N<sub>2</sub>/PFCs were significantly decreased in comparison with the dense film of 6FDA-BAAF. The decline of permselectivity was caused by small defects on the membrane surface. Coating silicone rubber was effective to restore the permselectivity and increased to 250 for N<sub>2</sub>/CF<sub>4</sub> pair at 25 °C.

To fabricate a highly selective membrane, preparation of molecular sieve carbon membranes was tried by carbonization of 6FDA-BAAF polyimide and others. The carbonized polyimide hollow-fiber membrane exhibited high permselectivity for nitrogen and PFCs pairs, for example, ISF of 60,000 for N<sub>2</sub>/SF<sub>6</sub> pair and of 4,000 for N<sub>2</sub>/CF<sub>4</sub> and N<sub>2</sub>/HFC-134a pairs at 100 °C. A high permeable carbon membrane would be also possible when a trimethyl silyl PPO membrane was carbonized.

Analysis of back diffusion mixing predicted that a membrane module of which mixing parameter was bigger than 100 could perform high separation with keeping a high permselectivity of membrane itself.

The results of process simulation for the recovery SF<sub>6</sub> showed that one stage separation with the membrane of ISF=50 to 200 could not recover more than 90% and two unit series configuration could recover efficiently at high rate. Using carbon membranes with highly permselectivity a one-stage membrane separation could recover almost 100% SF<sub>6</sub> with a smaller energy consumption of 0.23kWh/mol. The energy cost is less than 1% of commercial price of SF<sub>6</sub>. Carbon membranes demand large membrane area because of their small gas permeances. Simple series connection of polymer and carbon membranes mitigates the membrane area demanded with almost the same recovery and energy consumption as the carbon membrane itself.

##### (2) Development of the process for recovery and regeneration of fluorinated global warming compounds with hydrates

Through an overall investigation of experimental results, it was verified that more than

99mol% HFC-134a could be obtained from gas mixtures after hydrate formation and subsequent dissociation processes. In most cases, the operation can be carried out at pressures lower than 1.0MPa.

The hydrate formation kinetics experiments on the ternary HFC-134a + N<sub>2</sub> + water mixtures were carried out at 278.15K and 0.4MPa. The change in the vapor phase compositions was very rapid early on in the growth period, slowed down gradually, and stopped after about 60 min. Even though it takes about 1 hour to reach an equilibrium state at each condition, 20-30 minutes would be sufficient for hydrate formation under each step of the actual process because more than 80 % of the composition difference between the initial and final equilibrium states can be achieved within 20 minutes.

The HFC-134a separation process using gas hydrate formation has several advantages from an operational point of view. The operation can be conducted over mild temperature (275-285K) and low pressure (0.1-2.7MPa) ranges, depending on the vapor phase compositions. In most cases, the operation can be carried out at pressures lower than 1.0MPa. The separation medium consists only of water and no additive is needed to lower the hydrate formation pressure. Therefore, this separation process is very environmentally friendly.

### (3) Development of the technology decomposing fluorinated global warming compounds with nonthermal plasma

Without catalysts, humidity and gaseous oxygen suppress the decomposition of fluorinated global warming compounds. However, use of **SDR** or **SFR** with MnO<sub>2</sub> in the presence of water gives higher conversions of HFCs and higher yields of CO<sub>2</sub> in air.

In the reactions of HFCs, higher reactor energy densities and higher conversions of HFCs were obtained with the triangle waveform than that of sine at the same applied voltages in the range of 50Hz to 20kHz. However, the difference in the reactor power consumptions for both the waveforms was small at 50Hz, and comparable reactor power consumptions were obtained with the sine waveform at 50Hz and higher frequencies by applying maximum applied voltages under those conditions. Practically, it is recommended to select pertinent frequency and applied voltage for sine ac power.

Hybridization of **SDR** or **SFR** and catalysts such as MnO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub>, and AlPO<sub>4</sub> promoted the decomposition of fluorinated global warming substances. Oxygen atoms, which are formed on the surface of MnO<sub>2</sub> from ozone, facilitate the oxidative decomposition of HFCs. TiO<sub>2</sub>, which is activated by plasma emission, is considered to act as a photocatalyst. On the other hand, AlPO<sub>4</sub> promotes their decomposition in N<sub>2</sub> via the through-bond interaction between them. The synergy of nonthermal plasma and AlPO<sub>4</sub> lowers the energetic barrier for the cleavage of C-F bond in HFCs. The additive effect of the above catalysts depended on the chemical structures of fluorinated global warming compounds.

Use of multi-modal catalysts comprising  $\text{MnO}_2$ ,  $\text{TiO}_2\text{-SiO}_2$ , and  $\text{AlPO}_4$  is practically recommended to increase the energy efficiency in the decomposition of fluorinated global warming compounds.

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