

Highly Efficient Decomposition of CF₄ Gases by Combustion

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Abstract: PFCs (Perfluorocarbons) gases have a high global warming potentials (GWP) and a long lifetime in the atmosphere. It is difficult to decompose these gases due to their tetrahedral structure arising from the strong C-F bonds. The purpose of this study was to develop a low-cost combustion system assisted with catalyst to effectively destruct a PFC gas, CF₄. Experimental results showed the decomposition efficiency of CF₄ even reach 99.9% in this system. In addition, the effect of the concentration of CF₄, the amount of fuel gas, oxygen concentration and an alumina-phosphate catalyst on the destruction efficiency were also evaluated.

Keywords: Catalyst; CF₄; Combustion; Decomposition

1. Introduction

Perfluorocarbons are widely used in the semi-conductor industry, process cleaning solvents and fire suppression agent. Anthropogenically generated perfluorocarbons are considered as greenhouse gases because they are particularly effective at absorbing radiation, especially in this atmospheric window over the range from 1000-1360 cm⁻¹. This latter radiation is emitted from the Earth's surface and absorbed by such perfluorocompounds, which then reemits this infrared radiation towards earth, then results in forced global temperature increases. Especially, PFCs are not easily be decomposed because of their stable C-F and tetrahedral structure. Table 1 illustrates that these gases are strong infrared radiation absorbers relative to CO₂ and have long atmospheric lifetimes making them significant greenhouse gases and potential contributors to global warming. In 1997, PFCs became one of the important targets for reduction in COP3 (United Nations Framework Convention on Climate Change Conference of the Parties-3, also referred to as the Kyoto Protocol). On April 23, 1999, the WSC (World Semiconductor Council) announced its goal to reduce PFC emissions by 10% or more by the year 2010 [1].

The control and regulation of such anthropogenic greenhouse gas emissions, and the decrease of subsequent forced global warming has been hot wave. As abatement methods for PFCs, the chemical adsorption, catalyst, plasma and combustion methods has been used.

The disposal of perfluorocompounds and chlorofluorocarbons by plasma has been reported by many researchers. Hou et al. reported that more than

85% CF₂Cl₂ and 95% CF₂ClBr can be decomposed by dielectric barrier discharge after 10s discharge under normal atmospheric pressure. The main products were CF₂O, Cl₂ and Br₂[2]. The study of Kuroki revealed that complete CF₄ decomposition was achieved by plasma at 0.19 NL/min with the power of 1.2 kW when CF₄ concentration was 52%. However, the reactor was damaged possibly by local heat generation when the power exceeds 1.2 kW. Moreover, CF₄ decomposition efficiency depended on the power, the flow rate, and the quantity of O₂ addition[3]. Microwave plasmas at 2.45 GHz frequency operated at atmospheric pressure in synthetic gas mixtures containing N₂ and CF₄ are investigated experimentally by Marilena et al.[4]. It was found that the destruction and removal efficiencies of CF₄ up to 98% had been achieved using 1.9 kW of microwave power at 16 L/min total flow rate. How and Rung [5] investigated the technological feasibility and chemical kinetics of carbon tetrafluoride (CF₄) decomposition with tandem packed-bed plasmas (TPBPs). They claimed that the addition of Ar was beneficial to CF₄ decomposition. The effect of packing dielectric materials on CF₄ abatement is in the order of BaTiO₃>Al₂O₃>glass pellets, being correlative with their dielectric constants. The main shortcoming of plasma technology is its high operation cost.

Combustion is the most developed technology. A combustor equipped with natural gas or hydrogen injection system has demonstrated a greater than 90% abatement efficiency for C₂F₆, NF₃ and SF₆, but poor for CF₄ abatement possibly due to its high stability[6]. C-F bond is extremely high, about 486 KJ/mol, which can not be broken unless the reaction temperature is above 1600 °C[7]. Motorola also tested an inward fired burner utilizing methane fuel for CF₄ abatement. In Motorola testing, a CF₄ destruction efficiency of greater than 90% was achieved.

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Takizawa et al[8] experimentally investigated the combustion blends of R-152a and nonflammable fluorothanes (R-134a, R-125, and R-116) by means of combustion product analysis and burning velocity measurement. Combustion product analysis showed that, when the blend had insufficient hydrogen atoms to react with fluorine atoms to produce HF, the excess fluorine atoms produced COF₂ and CF₄ as combustion products.

However, the cost associated with fuels and solution used for scrubbing byproducts (as HF) is expensive when combustion is applied to decompose CF₄.

Catalyst decomposition is another practical alternative method for destructing PFCs or HFCs. Takita et al. and Bahy et al.[10] reported that that CF₄, the most stable compound in PFCs, was decomposed by the hydrolysis reaction at 973K on selected metal phosphate catalysts such as aluminum phosphate and its mixtures with rare earth metal phosphates. However, catalyst decomposition is limited by its durability because the catalyst always has to be exposed to the highly reactive HF and water at a temperature higher than 873 K.

In this paper, we developed a new CF₄ treatment system with high temperature of combustion flame and catalyst. At the same time, the scrubbing water can be recycled in the system. Especially, the byproduct (HF) can be recovered by forming CaF₂.

Table 1. Global warming potential and life-time of major greenhouse effect gases

Compounds	Chemical Formula	Life [year]	GWP (20 years)	GWP (100 years)	GWP (500 years)
Carbon Dioxide	CO ₂	-	1	1	1
Methane	CH ₄	12	56	21	7
Dinitrogen Oxide	N ₂ O	120	280	310	170
CFC-11	CCl ₃ F	50	5000	4000	1400
CFC-12	CCl ₂ F ₂	102	7900	8500	4200
HCFC-22	CHClF ₂	13.3	4300	1700	520
HFC-134a	CH ₂ F-CF ₃	15	3300	1300	420
Tetrafluoromethane	CF ₄	5000	4400	6500	10000
Hexafluoroethane	C ₂ F ₆	1000	6200	9200	14000
Sulfur Hexafluoride	SF ₆	3200	1630	23900	34900

2. Experimental Apparatus And Procedure

The experimental system consisted of a stainless-steel reactor, burner, gas supply system, shower tower and reaction tank. The schematic diagram of the experimental apparatus was shown in Figure 1. Figure 2 was a schematic diagram of the burner, which had four gas

inlets (O₂, air, liquefied petroleum gas (LPG) or liquefied natural gas (LNG) and CF₄) and an electronic igniter. In this work, the ratio of the primary air to the secondary air was changeable. The reactants are air with oxygen. In test run 1 and 2, only air is used. However, air and oxygen are used in run 3. The length and diameter of the stainless-steel reactor were 0.6 m and 65 mm, respectively. The burners used in the experiment are KBSS-500(Kinoshitarika CO., Japan) and KBSS-800(Kinoshitarika CO., Japan). KBSS-500 is used for LNG, and KBSS is suit for LPG gas. Their length and diameter are 290 mm and 10 mm, respectively. A filament was located 5 mm above the burner to stabilize the flame. The temperature of flame was measured by a charge coupled device (CCD) image technique. In semiconductor industry, common concentration of CF₄ in the exhaust gases was generally less than 5%. Therefore, initial concentration of CF₄ was about 5% in the experiments. LPG/LNG was used as the fuel gas to produce a high temperature flame. LPG is composed of 98.1% propane, 0.7% ethane, 0.9% isobutene and 0.3% butane. LNG contains 89.9% methane, 5.62% ethane, 3.43% propane and 1.35% butane. The flow rate of each gas was controlled independently with mass flow controller (MFC). The alumina-phosphate catalyst was placed at the top in the reactor, with a bed thickness of about 10 mm.

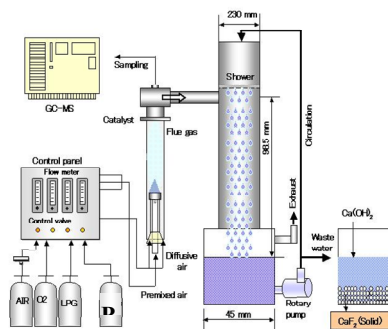


Figure 1 Schematic diagram of PFC gas destruction system

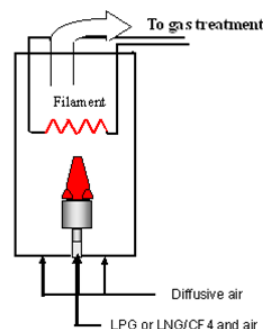
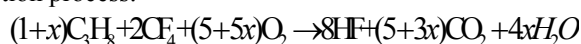


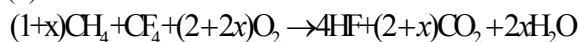
Figure 2 Schematic diagram of burner

In order to understand the decomposition mechanism, the thermal equilibrium calculation was carried with Factsage 5.4, as shown in Figure 3-4. In the calculation, F/H ratio varies from 0.1 to 1.9, the stoichiometry fuel/air ratio is kept 1.3. At the same time, the temperature (flame temperature) and pressure (101353 Pa) are kept constantly.

It is observed that there is water formation when F/H below 1.0 due to the combustion of LPG or LNG gas, while the reaction will not produce water after F/H above 1.0. At the same time, HF will be decomposed and form F or COF₂ as F/H above 1.0. However, the combustion of LPG or LNG will not occur when F/H is close to 1.0. On the basis of the calculated results, the following chemical reactions are proposed to describe the destruction process:



(1)



(2)

HF is highly toxic and corrosive, thus, the exhaust gas after PFCs combustion required immediate treatment. HF gas was reacted with NaOH solution in a shower tower, producing NaF. Then, the Na⁺ in the NaF solution was replaced with a Ca²⁺ by using Ca(OH)₂/CaCO₃ in the reaction tank, producing a fluorite, CaF₂. As we know, the solubility of CaF₂ is relatively low. Thus, CaF₂ can be recovered after separation and dried.

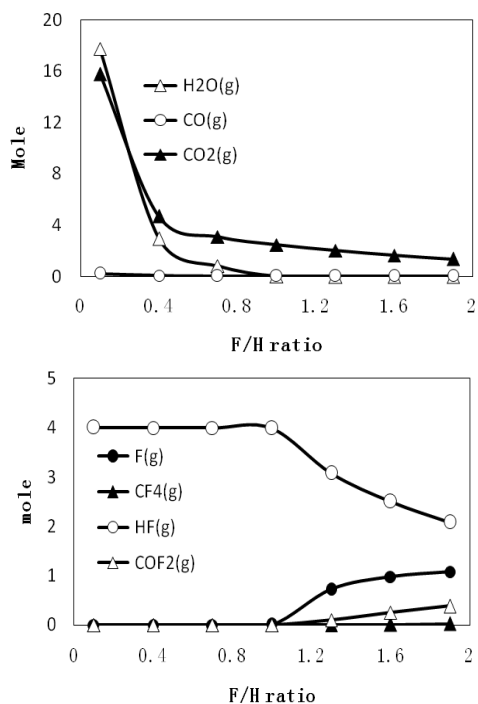


Figure 3 Dependence of species distribution with F/H for LNG combustion destructing CF₄

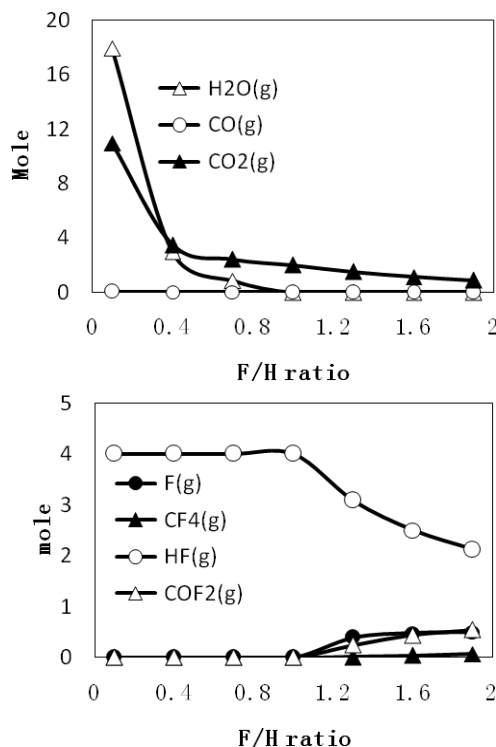


Figure 4 Dependence of species distribution with F/H for LPG combustion destructing CF₄

To measure the concentration of the remaining CF₄ in the treated gas, exhaust gas at the outlet of the high temperature reactor were passed into gas chromatography mass spectrometry analyzer (Shimazu QP2000) through the sampling pipe. The reproducibility deduced from sample repetition carried out in three samples is very good. Data deviation is lower than 0.4% for CF₄ measurement. The operation condition of the gas chromatography mass spectrometry is shown in Table 2. The destruction efficiency of CF₄ is defined with the following formula:

$$\text{Destruction efficiency}[\%] = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (3)$$

Table 2 Operation conditions of gas chromatography mass spectrometry

Equipment name	QP-2000 (Shimazu)
Capillary	Supel-Q(diameter: 32 mm; Length: 50 m)
Column temperature	120 °C
Injection temperature	180 °C
Detector temperature	180 °C
Carrier gas	He
Detector	Mass spectrometer
Split ratio	10
Pressure of injection	26.5 Kpa
Injection amount	0.5 ml

Here, C is the concentration of CF_4 measured by gas chromatography mass spectrometry in the exhaust gas, and C_0 is the initial concentration of CF_4 .

3. Results and Discussions

3.1. Effect of CF_4 Concentration

The effect of CF_4 initial concentration on the destruction efficiency was shown in Figure 5(run 1). In this test run, the initial concentration of CF_4 varied from 500 to 10000 ppm. The flow rate of LPG and LNG were 0.4 and 1.00 l/min, respectively. In this case, only premixed air was used and the stoichiometry fuel/air ratio was about 1.3. It was observed that 99% CF_4 destruction efficiency was achieved when CF_4 concentration is below 500 ppm. When LNG was fuel, the destruction efficiency sharply decreased at CF_4 concentration range of 1000-2000 ppm. While CF_4 concentration was higher than 2000 ppm, the decomposition efficiency appeared to be independent of the initial concentration. As for the case of LPG, the destruction efficiency gradually decreased with the increase of initial CF_4 concentration. In addition, the destruction efficiency for LPG was larger than that of LNG, which meant the destruction efficiency of equation (1) was greater than that of equation (2). The above phenomena may be attributed that the flame temperature is enough high to destroy the C-F bonds. The flame temperature of LPG and LNG are 2100 and 1930 °C, respectively.

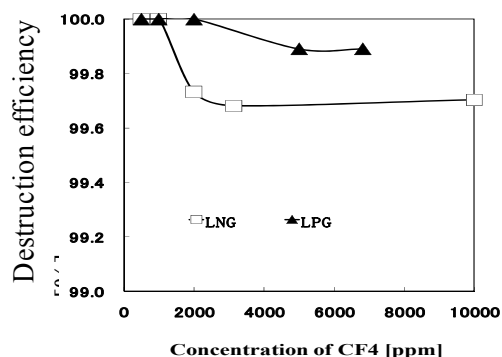


Figure 5 Dependence of destruction efficiency with the concentration of CF_4

- Effect of the catalyst

The effect of the catalyst, alumina-phosphate developed by ourselves, on the destruction efficiency of CF_4 was measured(run 2). In this case, only premixed air was used and the stoichiometry fuel/air ratio was about 1.3. The catalyst was prepared simply by impregnating phosphate such as $(NH_4)_2HPO_4$ and H_3PO_4 on Boehmite ($\gamma-AlOOH$), followed by drying at 100°C for 5 h and calcining at 700°C for 10 h.

Figure 6 demonstrated that the catalyst had no significant effect on CF_4 destruction efficiency at a low CF_4/LPG ratios. The destruction efficiency was higher

than 99.9% in the presence and absence of catalyst when CF_4/LPG ratios was below 3. However, CF_4 destruction efficiency was sharply decreased with the increase of CF_4/LPG ratios when CF_4/LPG was above 3 in the absence of catalyst. At the same time, catalyst could promote CF_4 decomposition by the following reactions[6]:

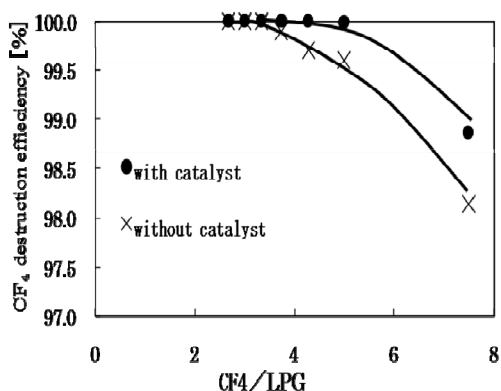
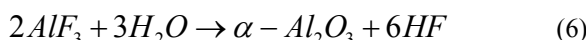
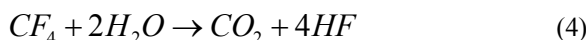


Figure 6 Effect of catalyst on destruction efficiency at different CF_4/LPG ratio



Although it was mentioned in the literature that the activity of alumina-phosphate catalyst would be decreased because HF eroded the surface of catalyst[11], this phenomena was not found in our experiment. It was assumed that most of CF_4 in our study was destroyed by combustion method and there was not a large amount of water in the flue gas.

3.2. Effect of Oxygen Concentration

Figure 7 compared the CF_4 destruction efficiency under the premixed and diffusive combustion(run 3). In this test run, the reactants was modeled through compressed gases (CF_4 , O_2 , N_2 and Ar) according to the requirement of experiment, and the stoichiometry fuel/air ratio was about 1.3. In the diffusive flame, the destruction efficiency was only 56% even the oxygen concentration was 100%. In the case of premixed-diffusive flame, we fixed the premixed oxygen concentration (12.5%), and changed the diffusive oxygen from 20 to 100%. It was found that the destruction efficiency was significantly increased from 0 to 63% when the diffusive oxygen concentration shifted from 20 to 40%, then the diffusive oxygen concentration had a slight influence on the destruction efficiency. The two reasons can be applied to explain the above phenomena: the premixed flame temperature is higher than the diffusive flame temperature, and the flame temperature increases with O_2 concentration. Another reason is that O_2 or O atoms could react

with CF_4 and its fragments, such as CF_x , then removing C atoms by forming CO_2 , CO , and COF_2 [12].

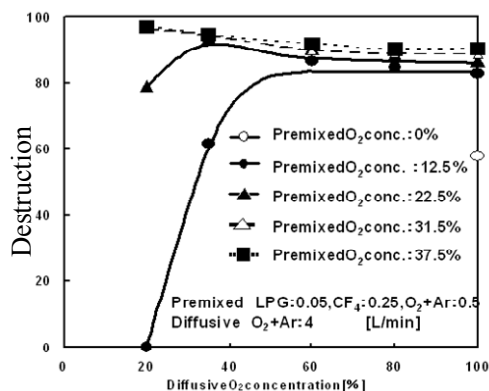


Figure 7 Dependence of destruction efficiency on O_2 concentration

The CF_4 destruction experiments under different premixed and diffusive oxygen concentrations were also carried out. When the premixed oxygen concentration was above 22.5%, the CF_4 destruction efficiency was slightly decreased with the increase of diffusive oxygen concentration. For example, the CF_4 destruction efficiency was 94% at 20% premixed oxygen concentration and 37.5% diffusive oxygen concentration, which was gradually decreased to 90% when the diffusive oxygen concentration was increased to 60%. The phenomena could be explained by the reason that there was difference in heat capacity between O_2 and Ar (and eventually difference in emissivity), which might affect the flame temperature and CF_4 decomposition efficiency.

4. Conclusions

CF_4 destruction experiments were performed in a hybrid system combining catalyst with combustion. The following results were obtained:

CF_4 destruction efficiency was greater than 99.9% in the system.

The destruction efficiency was decreased with the in-

crease of initial CF_4 concentration.

The catalyst can promote CF_4 destruction efficiency when CF_4 /LPG ratio is above 4.0.

The destruction efficiency of CF_4 was in proportion to oxygen concentration in the premixed air. However, too high oxygen concentration in the diffusive air had not significant impact on the destruction process.

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