

Decomposition characteristics of SF₆ in an electrical tube furnace and a pilot system by combustion

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Abstract—Sulfur hexafluoride (SF₆) is widely used in a variety of industrial processes and commercial products. However, this chemically stable gas is one of the most potent greenhouse gases (GHGs) contributing significantly to global warming. Therefore, to reduce greenhouse gas such as SF₆, a new eco-friendly, economic, and stable treatment technology is required. In this study, the thermal decomposition characteristics of SF₆ were investigated using a laboratory scale electrical tube furnace reactor and combustion-based pilot system. Based on these results, the SF₆ decomposition reaction order is around 1 and its activation energy (E_a) in the investigation temperature range is 238.04–257.18 kJ/mol. This value is used to calculate the reactor size when designing a commercial facility. Also, the experimental results of a combustion-based pilot system indicate that SF₆ supply location, reaction temperature, supplied concentration, and fuel/air ratio could affect SF₆ decomposition efficiency. The results demonstrate that a 99.9% decomposition efficiency could be achieved in the combustion.

Keywords: SF₆ (Sulfur Hexafluoride), Thermal Decomposition, Combustion, Decomposition Rate, Global Warming Gas

INTRODUCTION

SF₆ gas insulated equipment, such as gas insulated switchgear (GIS), gas insulated line (GIL), gas insulated transformer (GIT), gas circuit breaker (GCB) have been widely used in the power supply system of modern cities because of its small area, high security, reliable operation, and long maintenance cycle [1]. However, its global warming index is 23,900 times that of CO₂, and its lifetime in the atmosphere is 3,200 years [2]. The Korea Electric Power Corporation (KEPCO) consumes 80% of Korea's domestic SF₆ usage, and 6,033 tons are currently charged in their power facilities. From 2023, insulating gas is expected to be gradually replaced with eco-friendly gas. Since large amounts of SF₆ are to be disposed of annually from existing facilities, it is necessary to develop large capacity SF₆ decomposition technology for the near future.

SF₆ decomposition and pollution control technology neutralizes the decomposition gas after thermal decomposition of SF₆ at a high temperature. To maintain a high decomposition rate by controlling the reaction mechanism and to prevent by-products and recombination after decomposition, it is necessary to design a combustion reactor and a post-treatment system.

The decomposition methods of SF₆ are generally known as combustion, catalytic oxidation and plasma process [3]. The combustion method promotes decomposition in high temperature combustion reactors, which is advantageous when dealing with large amounts of gas. Catalytic oxidation chemically processes SF₆ under relatively low temperature conditions through catalytic reactions. The plasma process decomposes SF₆ in a high temperature and highly

reactive atmosphere caused by plasma. The way is suitable for small-scale processing capacity and has low reaction by-products, but requires process design, plasma generation, and high efficiency processing technology to improve economic benefits. It is known that SF₆ can be effectively processed if heat sources are maintained at more than 1,200 °C in sufficient firing furnaces with the simultaneous presence of water vapor. Although combustion methods were widely used to treat waste, there were few reports on decomposing SF₆ by combustion [4,5].

In this study, we first conducted thermal decomposition of SF₆ using an electrical tube furnace reactor to identify its thermal decomposition characteristics. We then identified the characteristics of decomposition and pollution control by establishing a combustion-based apparatus.

EXPERIMENTAL

1. Electrical Tube Furnace Reactor

Before testing the combustion based SF₆ decomposition system, experiments were carried out using an electrical tube furnace reactor with thermocouples and mass flow controllers. The configuration and specifications are shown in Fig. 1 and Table 1. Before the experiment, the tube furnace reactor was electrically heated to a predetermined temperature. SF₆ was mixed with argon and fed into the reactor. In these runs, the reactor temperature was in the range of 1,334–1523 K, and the flow rate was about 1,500–2,500 cc/min, as summarized in Table 2. After passing the reactor, the composition of exhaust gas was analyzed by Fourier transform infrared spectroscopy (FT-IR).

2. Combustion Based SF₆ Decomposition and Pollution Control Pilot System

The SF₆ decomposition by combustion experiment was carried

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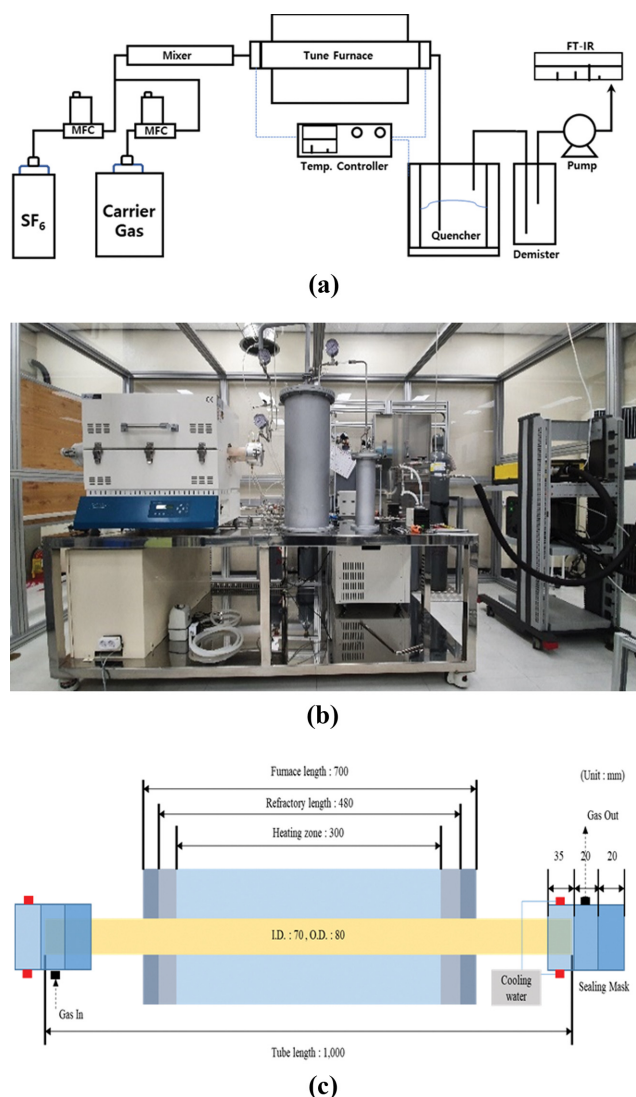


Fig. 1. Electrical tube furnace reactor. (a) Schematic diagram of the electrical tube furnace facility, (b) Electrical tube furnace facility, (c) The size of tube furnace reactor.

Table 1. System configuration

Items	Specifications
Tube furnace	Max. 1,500 °C (Quartz)
Quencher	Dip tube type/20 liter
Pump	Max. 5.5 liter/min

Table 2. Experiment of conditions

Conditions	Range
Temperature (K)	1,334, 1,430, 1,523
SF ₆ concentration (vol%)	3.0, 4.0, 5.0
Flow rate (cc/min)	1,500, 2,000, 2,500
Tube material	Quartz

out using a pilot system consisting of a combustion reactor, a burner, a quencher, a scrubber, supply tanks, gas supply systems (Induced

Table 3. System configuration

Items	Specifications
Mass flow controller	SF ₆ , Air, C ₃ H ₈
Combustor	Max. 1,300 °C/ Length: 900 mm
Quencher	1,300 liters (Nozzle: 6 EA)
Scrubber	200 liters (Nozzle: 4 EA)
Neutralize tank	100 liters
Storage tank	200 liters

Table 4. Experimental conditions

Conditions	Range
SF ₆ supply location	LPG line, Air line, Combustor wall
Temperature (°C)	790-890
SF ₆ supply (liter/min)	5, 8, 11
Flow rate (liter/min)	200.0-292.8
Excess air ratio (%)	10-60

Table 5. Specifications of equipment

Items	Specifications
QMS	Mass range: 1-200 amu
	Detection limit: 5 ppm
	Detector: Faraday cup, Secondary Electron Multiplier
FT-IR	Peltier cooled HgCdTe (MCT) detector
	Resolution: 4 cm ⁻¹
	Spectrum range: 900-4,200 cm ⁻¹

Draft (I.D.)) fan and control systems. The configuration and specifications are shown in Fig. 2 and Table 3.

The schematic diagram of the burner is shown in Fig. 3. The length and diameter of the burner were approximately 230 mm and $\Phi 143.2$, respectively. SF₆ and fuel (LPG, Liquefied Petroleum Gas) were fed into the burner in a mixture and air was fed separately at the determined ratio, followed by absorption in a quencher and scrubber to remove HF and SO₃. The experimental conditions of the system are summarized in Table 4.

3. Quantitative Measurement

After passing the system, the flow rate of the exhaust gas was measured by a Quadrupole Mass Spectrometer (QMS) using helium (He). QMS is the simplest of mass spec instruments. QMS consists of an ionizer (bombardment by electrons from a hot filament), an ion accelerator, and a mass filter consisting of four parallel metal rods. Two opposite rods have an applied potential of $(U + V \cos(\omega t))$ and the other two rods have a potential of $-(U + V \cos(\omega t))$, where U is a dc voltage and $V \cos(\omega t)$ is an ac voltage. The applied voltages affect the trajectory of ions traveling down the flight path centered between the four rods. For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter, and all other ions are thrown out of their original path. The mass spectrum was obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied.

The composition of exhaust gas was analyzed by the FT-IR in real time. The specifications of the equipment system are summa-

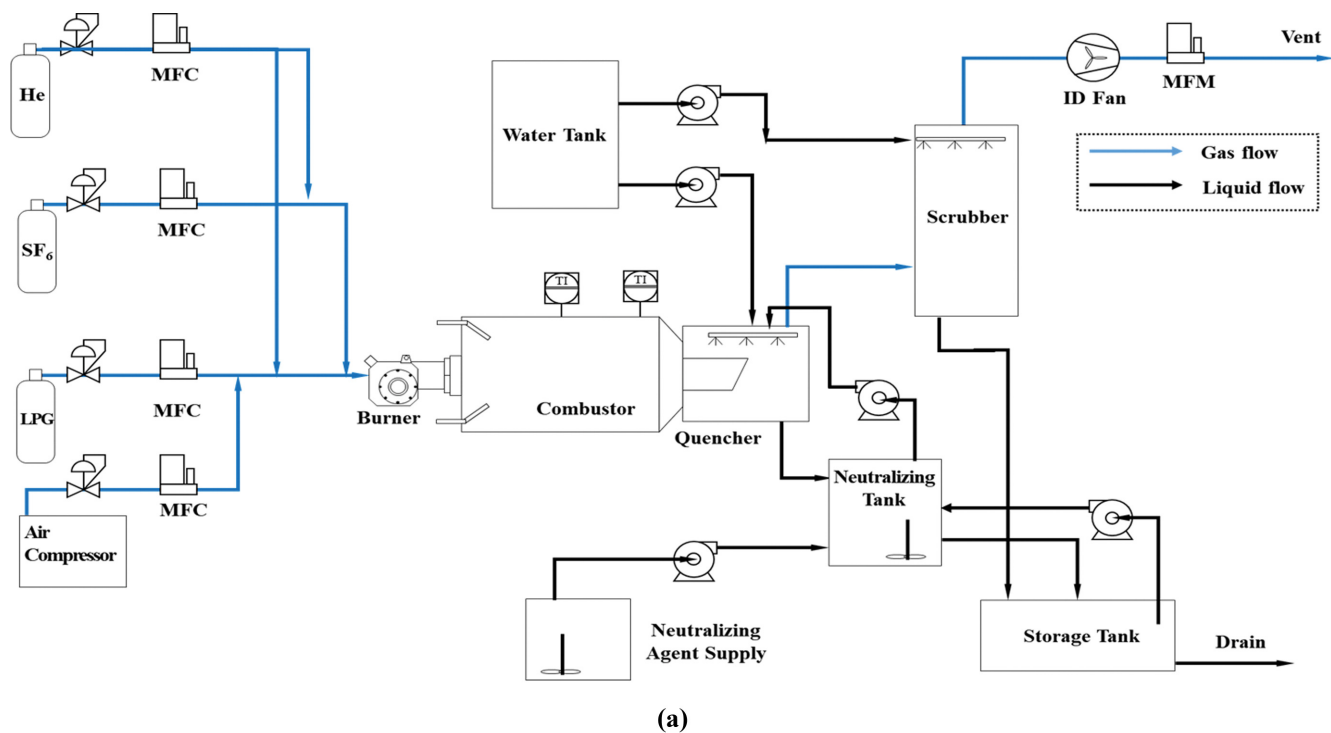
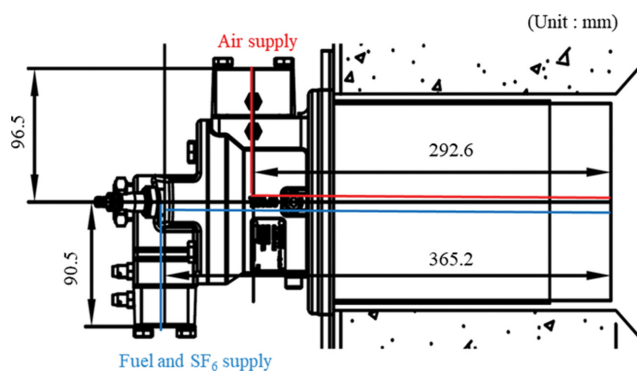


Fig. 2. Combustion based SF₆ decomposition and pollution control system. (a) Schematic diagram of the pilot system, (b) Photograph of the pilot system.



rized in Table 5.

In this study, SF₆ decomposition performance is described as the SF₆ decomposition rate as follows:

$$\text{SF}_6 \text{ decomposition rate (\%)} = (1 - (\text{SF}_6 \text{ in outlet gas} / \text{SF}_6 \text{ in inlet gas})) \times 100$$

EXPERIMENT RESULTS OF ELECTRICAL TUBE FURNACE REACTOR

Thermal decomposition experiments were conducted on variables according to reaction temperature, gas flow rate, and SF₆ initial concentration. Our experiment used a tube reactor made of

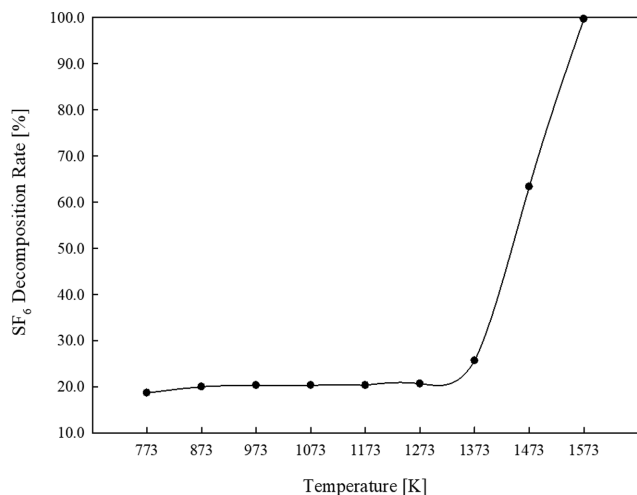


Fig. 4. Effect of temperature on SF₆ decomposition.

quartz material instead of the initial alumina reactor. In the alumina reactor, the etched alumina caused line plugging during the experiment. If an alumina reactor is used, it is necessary to establish a safety system to prevent accidents by installing a pressure measuring instrument or process safety valves that can recognize line plugging.

1. SF₆ Pyrolysis Characteristics

We first analyzed the concentration of SF₆ by temperature change every 100 K between 773–1,573 K to check the characteristics of thermal decomposition.

As shown in Fig. 4, the phenomenon of rapid decomposition in the vicinity of 1,400 K can be seen. When reaching 1,600 K, a decomposition of over 99% can be confirmed.

These experimental results simply consider the properties of decomposition through thermal decomposition without the addition of water mentioned in the literature [6], and if water is added, it can decompose at a lower temperature [7].

2. Effect on SF₆ Decomposition Rate under Different Conditions

The dependence of SF₆ decomposition rate on temperature under initial SF₆ concentration and gas flow rate is shown in Fig. 5. The experimental results can be easily predicted; the higher the temperature and residence time and the lower the initial SF₆ concentration, the higher the decomposition rate as a result. However, the purpose of these experiments is to determine how much influence each variable has. The increase of the initial SF₆ concentration has a negative effect on the decomposition rate. At a 2,000 cc/min gas flow rate and a temperature of 1,473 K, the decomposition rate decreases from 63 to 53% when SF₆ concentration increases from 3 volume% to 5 volume%. The increase of the gas flow rate also has a negative effect on the decomposition rate. At 1,473 K and 3% of the initial SF₆ concentration, the decomposition rate decreases from 77 to 51% when the gas flow rate increases from 1,500 to 2,500 cc/min. Among these variables, the temperature has the greatest influence. At a 2,000 cc/min gas flow rate and 3% initial SF₆ concentration, the decomposition rate increases from 25 to 99% when the temperature increases from 1,373 to 1,573 cc/min. To obtain a decomposition rate of 99% or higher, it is preferable to design a reac-

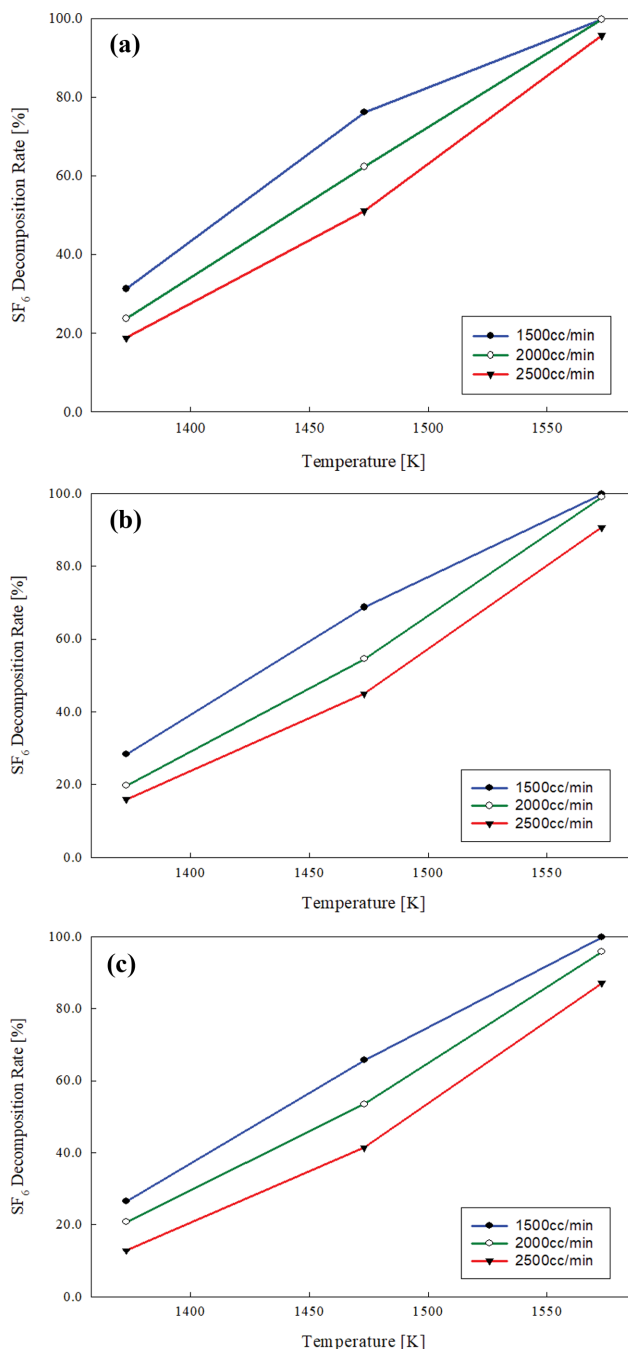


Fig. 5. SF₆ decomposition rate as a function of temperature under different initial concentrations and gas flow rates. (a) SF₆ initial concentration of 3%, (b) SF₆ initial concentration of 4%, (c) SF₆ initial concentration of 5%.

tor by setting a gas flow rate or an initial SF₆ concentration after first setting an applicable temperature range. As shown in Fig. 5, the effect of each variable can be confirmed under various conditions. The small difference in influence by variables at high temperatures can be assumed because conditions of higher temperatures have already achieved a near 100% decomposition rate.

3. Kinetic Characteristics of SF₆ Decomposition

The decomposition efficiency of SF₆ can be described by the fol-

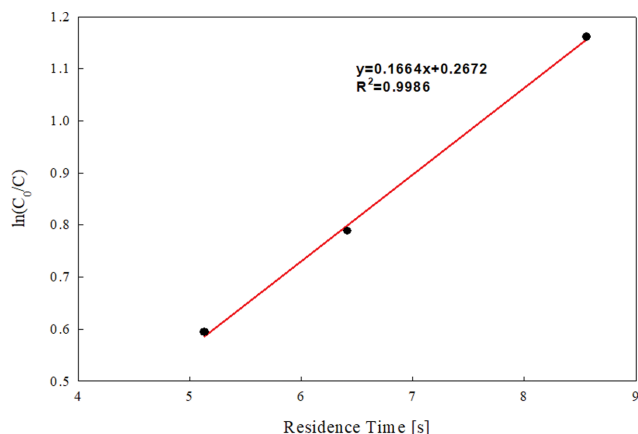


Fig. 6. Dependence of the reaction rate on residence time.

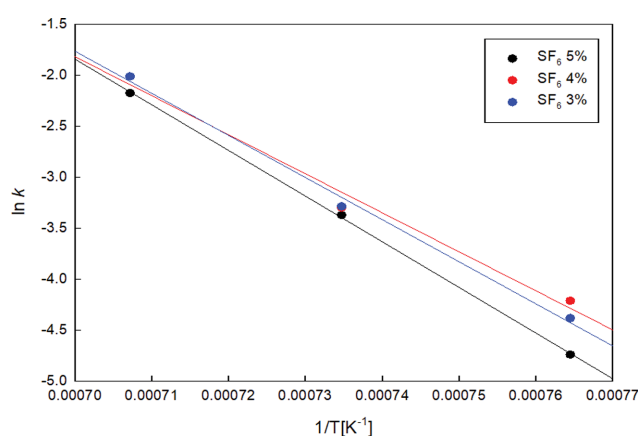


Fig. 7. Dependence of $\ln k$ on $1/T$.

lowing equation:

$$-\frac{d[C]}{dt} = k[C]^n$$

where C is the SF₆ concentration at time t , k is the specific reaction rate constant, and n is the order of the reaction.

In Fig. 6, the dependence of the reaction rate on the residence time is shown. The linear dependence indicates that the reaction order is approximately 1. Thus, the equation can be rearranged as

$$k = -\frac{1}{[C]} \frac{d[C]}{dt}$$

The reaction rate constant may follow the Arrhenius equation,

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

where A is the frequency factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature.

After some rearrangement we obtain

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

The slope and intercept of the plot $\ln k$ vs. $1/T$ in Fig. 7 were used

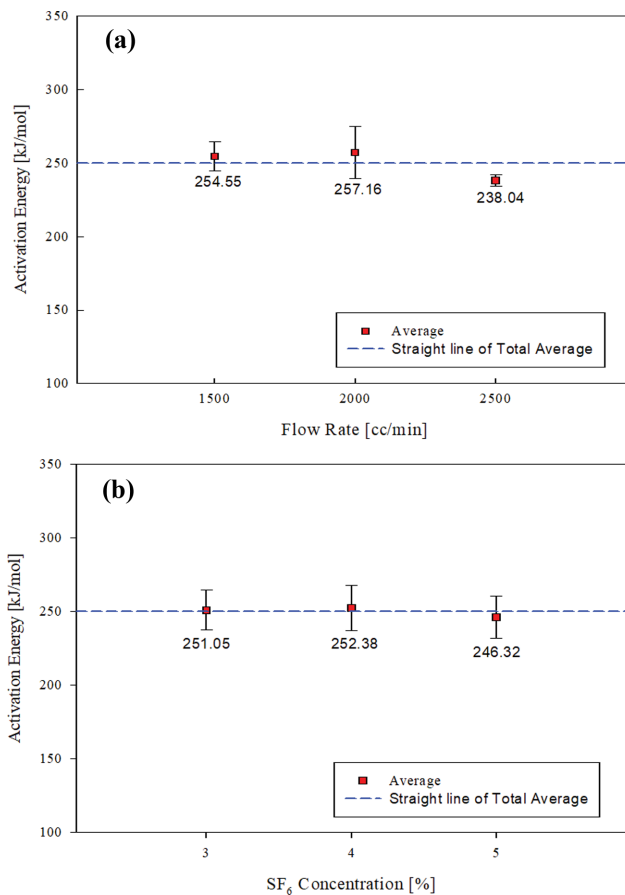


Fig. 8. Activation energy on the temperature and the initial concentration of SF₆. (a) The activation energy on the temperature, (b) The activation energy on the initial conc. of SF₆.

to calculate the kinetic parameters of the reaction.

In this study, the activation energy was obtained as 238.04–257.18 kJ·mol⁻¹ based on argon for the carrier gas, as shown in Fig. 8 and Table 6.

Lyman [8] revealed that the activation energy was 382 kJ·mol⁻¹. Tsang and Herron [9] found that the activation energy was 422 kJ·mol⁻¹. Han [10] also found that the activation energy was 354 kJ·mol⁻¹ based on helium and 371 kJ·mol⁻¹ based on argon. Mi et al. [11] also obtained that the activation energy of HFC-134a was 300.05 kJ·mol⁻¹ and a frequency factor of -2.96×10^{14} . Hayashi et al. [12] stated that the activation energy of C₂F₆ was 313.2 kJ·mol⁻¹.

Through these basic experiments, it is possible to roughly estimate the size of the reactor required for SF₆ decomposition. In the commercial SF₆ decomposition system, combustion reactions using LPG are applied. H₂O generated during combustion reaction participates in the decomposition and achieves a better decomposition rate. The local adiabatic flame temperature is also higher during combustion than the measured internal temperature in an electric tube furnace reactor, so H₂O is not consistent with the experimental conditions. Despite these restrictions, it can be applied to the commercial system design in consideration of the safety margin and the trend through these electric tube furnace reaction characteristics experiments.

Table 6. Experimental results of activation energy

Conc. SF ₆ (%)*		Feed flow rate (cc/min)	T (K)	Ea (kJ/mol)
Input	Output			
2.9	1.99	1,500	1,334	242.0
	0.69		1,430	
	0.01		1,523	
3.8	2.73	1,500	1,334	255.8
	1.19		1,430	
	0.01		1,523	
4.7	3.47	1,500	1,334	265.8
	1.62		1,430	
	0.01		1,523	
2.9	2.24	2,000	1,334	270.3
	1.11		1,430	
	0.01		1,523	
3.9	3.09	2,000	1,334	269.0
	1.75		1,430	
	0.04		1,523	
5.0	3.94	2,000	1,334	232.2
	2.31		1,430	
	0.21		1,523	
3.0	2.42	2,500	1,334	240.9
	1.46		1,430	
	0.13		1,523	
4.0	3.32	2,500	1,334	232.3
	2.18		1,430	
	0.37		1,523	
4.8	4.18	2,500	1,334	240.9
	2.81		1,430	
	0.62		1,523	

*It was measured by FT-IR.

SF₆ DECOMPOSITION CHARACTERISTICS BY COMBUSTION IN A PILOT SYSTEM

To evaluate the performance of the SF₆ decomposition pilot system, we carried out three kinds of experiments, as explained below.

1. Effect of SF₆ Supply Location

To assess decomposition efficiency according to the SF₆ supply locations, SF₆ was supplied in three different locations (fuel supply line, air supply line, wall of combustor supply line) to identify the decomposition rate assessment under the following conditions: 1,273 K, 7 liter/min for SF₆ supply, 12 liter/min for fuel (LPG) supply, and 375 liter/min for air. The results of the experiment are shown in Fig. 9.

During the experiment, it was possible to obtain a high decomposition rate when exposed to a high flame temperature by supplying the combustor to the center with a supplying fuel nozzle. Conversely, supplying SF₆ along the combustor wall from 650 mm at the end of burner tip resulted in a lower decomposition rate than in other cases. This implies that, when scaling up, it will be advan-

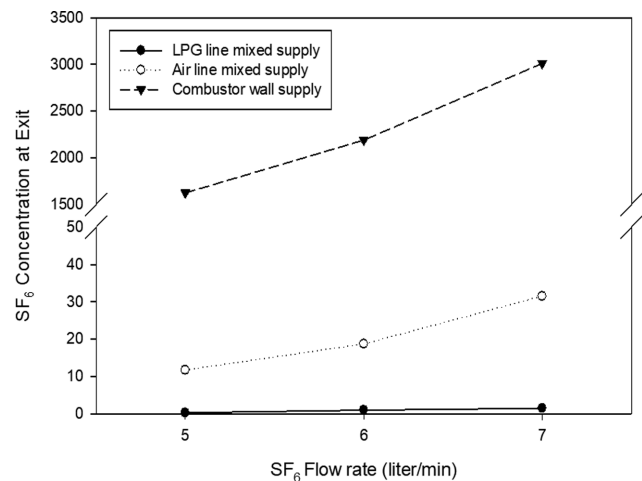


Fig. 9. SF₆ concentration at exit according to feed location of supply.

Table 7. Experimental results of SF₆ decomposition rate according to temperature

Temp. (°C)	Flow rate (liter/min)		Conc. SF ₆ **		Decom. rate (%)
	Inlet	Outlet*	Inlet (%)	Outlet (ppm)	
1,063	197.0		2.54	19.51	99.90
	200.0	170	4.00	59.03	99.81
	203.0		5.42	>200	-
1,113	235.2		2.13	8.8	99.95
	238.2	208	3.36	21.4	99.93
	241.2		4.56	46.5	99.89
1,163	286.8		1.74	8.1	99.95
	289.8	260	2.76	13.7	99.96
	292.8		3.76	28.8	99.93

*Measured by QMS (Quadrupole Mass Spectrometer)

**measured by FT-IR (Fourier Transform Infrared Spectroscopy).

tageous to apply the method of supplying fuel with or around the fuel supply line.

2. Effect of Temperature and SF₆ Supplied Concentration on Combustion Furnace

To find the effect of each operating variable of the temperature and supplied SF₆ concentration, experiments were conducted at a 28% of excess air ratio while changing the temperature from 1,063 to 1,163 K and the supplied SF₆ concentration from 3 to 5 volume%. As predicted, the lower the concentration of SF₆ supplied and the higher the temperature, the higher the obtained decomposition rate, as shown in Table 7.

When 5 volume% of SF₆ was supplied while the internal temperature of the combustion furnace was maintained at 1,063 K, a significantly lower decomposition rate than other conditions (i.e., a high SF₆ concentration at the output) was observed. Among the conditions conducted in these experiments, a high temperature was formed in the center of the front end of the combustion furnace, resulting in a perfect decomposition of 99.9% or higher. When the internal temperature was 1,113 K, the local adiabatic flame tem-

Table 8. Experimental results of SF₆ decomposition rate according to excess air ratio (at 1,143-1,163 K)

Inlet flow rate (liter/min)			Excess air ratio (%)	Flow* rate (liter/min)	Conc. SF ₆ **		Decom. rate (%)
SF ₆	LPG	Air			Inlet (%)	Outlet (ppm)	
5	8.8	234	10.0	275	2.02	2.69	99.99
		255	19.9	285	1.86	5.45	99.97
		273	28.4	290	1.74	15.60	99.91
		298	40.1	335	1.60	26.05	99.83
		319	50.0	345	1.50	38.30	99.74
		340	59.9	365	1.41	67.63	99.51

*Measured by QMS (Quadrupole mass spectrometer)

**Measured by FT-IR (Fourier transform infrared spectroscopy).

perature was calculated to be 2,009 K. It was confirmed that the currently established decomposition system could stably obtain the desired decomposition rate during operation under the condition shown in Table 7. In the case of the inlet flow rate in Table 7, the amount supplied through the mass flow rate (MFC) is arithmetically summed, and the outlet flow rate is measured using QMS. The difference between the two values is expected to reflect amounts of by-products, such as HF, SO_x generated during the reaction, removed through the neutralization reaction.

3. Effect of Fuel/Air Ratio

The effect of the ratio of fuel to air on the SF₆ decomposition efficiency was analyzed by changing the supply the amount of air under the conditions of 5 liter/min for SF₆ supply, and 8.8 liter/min for fuel supply. In the case of reactor temperature, the experiment was conducted in a range from 1,143 to 1,163 K because the excess air ratio tends to decrease when the amount of air changes. It was confirmed that the higher the excess air ratio based on 10%, the higher the SF₆ concentration measured at the outlet sided, as shown in Table 8 and Fig. 10. Nevertheless, a decomposition rate of 99% or more could be confirmed. These results can be reflected in the review of the ratio of excess air that can be used for reactor temperature control when the temperature rises above a predetermined temperature, which may occur later during continuous operation. The reason why SF₆ at the outlet side increased, even though the total flow rate increased as excess air was supplied, is interpreted as

a decrease in residence time within a combustion furnace of a certain size. The flow rate in Table 8 refers to the total amount of gas supplied, and the SF₆ concentration on the inlet side was recorded as an arithmetic concentration value. The SF₆ concentration at the outlet side is a value measured using FT-IR.

CONCLUSIONS

The results of the experiments on the electrical tube furnace reactor demonstrate that the phenomenon of rapid decomposition without H₂O addition in the vicinity of 1,400 K can be seen and the decomposition reaction is first order. The activation energy was obtained at 238.04-257.18 kJ·mol⁻¹ based on argon for the carrier gas. Based on these results, the combustion reactor size can be calculated, and a combustion based SF₆ decomposition and pollution control pilot system was designed and constructed by applying the calculated values.

The combustion based SF₆ decomposition and pollution control pilot system achieved an SF₆ decomposition rate above 99%.

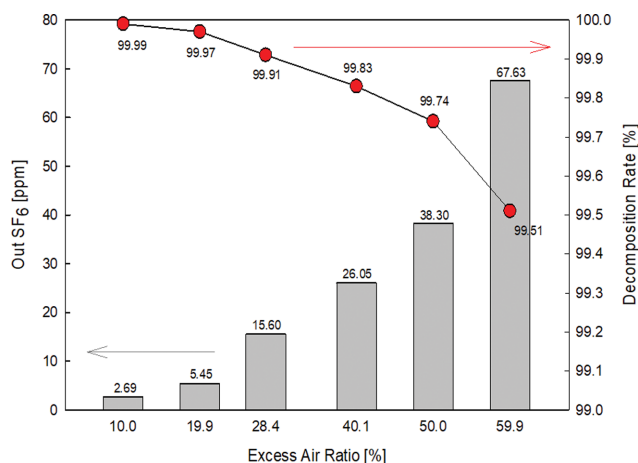
Using this system, the effects of the SF₆ supply location, temperature, SF₆ supply concentration, and fuel/air ratio were evaluated. In the case of SF₆ supply location, it was advantageous to supply fuel with or around the fuel supply line. And the lower the concentration of SF₆ supplied and the higher the temperature, the higher the decomposition rate could be obtained. It was confirmed that the higher the excess air ratio, the higher the SF₆ concentration measured at the outlet side. Under these characteristics, it is possible to control the decomposition condition of a pilot system.

ACKNOWLEDGEMENTS

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REFERENCE

1. F. Zeng, J. Tang and X. Zhang, *IEEE Trans. Dielectr. Electr. Insul.*, **24**, 367 (2015).
2. S. H. Han, H. W. Park, T. H. Kim and D. W. Park, *Clean Tech.*, **17**, 250 (2011).
3. J. B. Kim and J. Y. Ryu, *J. KSWM*, **37**, 546 (2020).

**Fig. 10. SF₆ decomposition rate according to excess air ratio.**

4. R. J. Van Brunt and J. T. Herron, *IEEE Trans. Dielectr. Electr. Insul.*, **25**, 75 (1990).
5. L. Qin, J. Han, G. Wang, H. J. Kim and I. Kawaguchi, *Sci. Res. Conf. Environ. Pollut. Public Health*, 126 (2010).
6. J. Diaz, A. M. Casanovas and J. Casanovas, *J. Phys. D. Appl. Phys.*, **36**, 1558 (2003).
7. F. Zeng, J. Tang, Y. Xie, Q. Zhou and C. Zhang, *Electr. Eng. Technol.*, **10**, 1787 (2015).
8. J. L. Lyman, *J. Chem. Phys.*, **67**, 1868 (1977).
9. W. Tsang and J. Herron, *J. Chem. Phys.*, **96**, 4272 (1992).
10. H. J. Han, *Diss. master dissertation*, Seoul National University of Technology, Seoul, Korea (2010).
11. T. Mi, J. Han, X. He and L. Qin, *Environ. Sci. Technol.*, **41**, 143 (2015).
12. S. Hayashi, W. Minami, T. Oguchi and H. J. Kim, *Kagaku Kogaku Ronbunshu*, **35**, 252 (2009).