A-6.1 Decomposition of Chlorofluorocarbons by Inductively-Coupled r.f. Plasma

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Abstract The inductively-coupled r.f. plasma reactors of 15 kW and 35 kW types were studied for the continuous decomposition of chlorofluorocarbons and other chlorinated carbons with water at atmospheric pressure. The reaction efficiency, products analysis, plasma state observations were investigated. CCl_2F_2 of 8.1 kg/h at maximum was decomposed on the 35 kW plasma torch.

Key Words: Plasma, Chlorofluorocarbons, Decomposition, Destruction

1. Introduction

Although ozone depleting substances (ODS) such as chlorofluorocarbons (CFCs), halons, and some chlorinated hydrocarbons will be phased out before the 21st century because of serious situation of the stratospheric ozone depletion on the Earth, there are large quantities of banked ODS in the world which should be decomposed urgently in the near future. CFCs, halons, and other ODS have been used since they are chemically and thermally stable. Therefore, ODS seems not easy to be decomposed, and research and development of the decomposition are desired.

2. Research Objective

An inductively-coupled radio-frequency plasma provides ultrahigh temperatures at atmospheric pressure. Even stable compounds like CFCs having impurities are decomposed rapidly and effectively as reported previously. This project aims at developing such a plasma technology for the decomposition of ODS though the plasma has advanced in the fields other than environmental technology, such as electronic semiconductor manufacturing, nuclear fusion, fine ceramics production, and so forth.

3. Thermodynamic Considerations

The calculations for the reaction of CFCs to yield raw materials such as Cl_2, HCl, F_2, HF, etc. are made using thermodynamic data. The results, for example, of CCl_3F are depicted in Table 1 and 2, in which main and side reactions are shown. The reaction pathway to give carbon, Cl_2, and ClF from CCl_3F alone is unfavorable because of an extremely small value of Kp (equilibrium constant). The substances having hydrogen and/or oxygen atoms are necessary for the decomposition of CCl_3F. The side reactions are, as shown in Table 2, disproportionation, dimerization, aromatization, and carbonylation, which sometimes lead to toxic compounds.

4. Research Method

The plasma reaction system consisted of radio-frequency power generator, plasma torch, CFCs supply, and tail-gas cleaning scrubber. As shown schematically in Fig. 1, the plasma torch is made of a tube (quartz or ceramic) winded by several-turned coil. Inside the tube CFCs and other reaction gases are passing. In this project we used two types of plasma, 15 kW and 35 kW plasma torches. In 15 kW output power torch, tube has a dimension of 38 mm (i.d.) and ca. 250 mm length. In 35 kW output power torch, diameter of an inner tube is 42 mm where an outer tube covers the inner tube and cooling water flows between them to prevent thermal damage due to plasma.

The reaction between CFCs and mainly water was investigated. Exhaust of acids, HF and HCl, were neutralized by a series of KOH and CaO scrubbers.

Products of CO and CO_2 were analyzed on an FID gas-chromatograph equipped with methanizer, or by NDIR. Unreacted CFCs were determined by an FID gas-chromatograph. Cl_2 in the tail gas was qualitatively measured by a gas-detection tube.

5. Results and Discussion

(1) Decomposition of CCl_3F

Figure 2 shows decomposition of CCl_3F as a function of input power of 15 kW plasma. As the power is increased, conversion of CCl_3F is increased. However, in the absence of water vapor the reaction produces carbonaceous materials and halogenated higher carbons. Detailed analysis, shown in Table 3, indicated that products in the gas-phase includes CF_4, $CClF_3$, CCl_2F_2, CCl_4, $C_2Cl_2F_2$, C_2Cl_3F, C_2Cl_4, $C_2Cl_3F_3$, $C_2Cl_4F_2$, and so forth. The carbonaceous materials in solid-phase revealed to contain Cl and F atoms and they may be formed through dimerization and cyclization reactions.

As seen in the figure, the reaction is promoted in the presence of water vapor. This phenomenon is in agreement with the thermodynamic considerations. The carbonaceous materials and the above-mentioned gaseous halogenated carbons disappears. At a feed ratio of $H_2O/CCl_3F = 2.0$ almost no by-products are produced. CO_2 and CO are detected quantitatively, and CO_2 becomes greater when water fed much larger. Material balances for carbon and chlorine atoms are 100% within experimental error. The balance for fluorine atom is quite poor, probably due to its reaction inside the chamber. Therefore, the reaction in the presence of water may be described as;

$$CCl_3F + 2H_2O = CO_2 + 3HCl + HF \qquad (1)$$

(2) Decomposition of Various ODS

Table 4 is the list of ODS decomposed by the 15 kW-plasma. Good efficiencies of destruction are obtained for $C_2Cl_3F_3$, $CHCl_3$, C_2HCl_3, and CCl_4. Lower efficiencies below 90% may be ascribed to detection errors because of lower feed concentrations.

(3) Characteristics of 35 kW Plasma

A 35 kW plasma was designed and its fundamental performance was investigated. We checked first the matching character of the plasma, in which 80% of argon was replaced by oxygen or steam under total flow of 105 L/min. The relationship between input voltage (Ep) and current (Ip) does not change greatly when oxygen or steam is fed. This fact expects optimistically that a larger power may establish a 100% steam plasma, which was in fact observed on a 100 kW plasma torch in our separate cooperative research project.

(4) Decomposition of CCl_2F_2 by 35 kW Plasma

Figure 3 is the results of the decomposition of CCl_2F_2 by the 35 kW plasma torch. The experiments were carried out at total flow of 105 L/min. All points have efficiencies more than 99.99%. As hydrogen is introduced, CO and unknown hydrocarbon (probably acetylene) is increased. On the other hand, when oxygen is added, the concentrations of CO and the hydrocarbon are reduced. Since the formation of CO is an indication of toxic substances such as dioxins and furans, we recommend that the reaction must be performed under oxidative conditions. The maximum capacity of the 35 kW plasma was 8.1 kg of CCl_2F_2 /h.

(5) Comparison of 35 kW Plasma with 15 kW Plasma

The 15 kW plasma gave 99.9% efficiency, permitted smaller steam ratio upto 44%, smaller total flow rate of 90 L/min, smaller capacity for CFCs decomposition, and so on. On the contrary, the 35 kW plasma gave 99.99% efficiency, permitted larger steam ratio upto 76 %, larger total flow rate of 185 L/min, larger capacity of 8.1 kg/h for CFCs decomposition. The reason for these facts comes from the volume of the torches, where diameters of 15 kW and 35 kW are 38 mm and 42 mm, respectively. The higher plasma energy is formed in relatively smaller volume of the 35 kW torch.

Using a 100 kW plasma torch, more than 50 kg of waste CCl_2F_2 and halon-1301 was decomposed at an efficiency more than 99.999% in the separate cooperative project.

Table 1

REACTION SCHEME	$\log K_p$	ΔH / J (K mol)$^{-1}$
$CCl_2F_2 + O_2 = CO_2 + 2ClF$	11.75	-143.50
$CCl_2F_2 + 2H_2O = CO_2 + 2HCl + 2HF$	41.03	-256.48
$CCl_2F_2 + 4H_2 = CH_4 + 2HCl + 2HF$	60.75	-84.13
$CCl_2F_2 + CH_4 + 2O_2 = 2CO_2 + 2HCl + 2HF$	181.46	-251.33
$2CCl_3F + 4CaO = 2CO_2 + 3CaCl_2 + CaF_2$	198.58	-1303.35
$CF_4 + 2H_2O = CO_2 + 4HF$	26.37	-269.38
$CClF_3 + 2H_2O = CO_2 + HCl + 3HF$	34.75	-258.83
$CCl_2F_2 + 2H_2O = CO_2 + 2HCl + 2HF$	41.03	-256.48
$CCl_3F + 2H_2O = CO_2 + 3HCl + HF$	45.05	-260.45
$CCl_4 + 2H_2O = CO_2 + 3HCl$	44.97	-273.66

Table 2

TYPE OF REACTION	log Kp			
	300K	1000K	1500K	6000K
Disproportionation $2CCl_3F = CCl_2F_2 + CCl_4$	1.32	0.07	-0.11	-0.38
Dimerization $2CCl_3F = C_2Cl_4 + 2ClF$	-72.5	-15.97	-6.22	4.09
Cyclization $6CCl_3F = C_6F_6 + 9Cl_2$	-599.16	-79.97	-7.65	
Carbonylation $CCl_3F + H_2O = COClF + 2HCl$	24.08	12.65	10.95	
$CCl_3F + 0.5O_2 = COClF + Cl_2$	30.67	12.19	9.46	

Table 3

Additives	None	None	H_2O	H_2O	O_2	H_2
(Molar ratio to CFC-11)	0.0	0.0	1.0	2.0	1.0	2.0
In-put power (kW)	7.2	13.5	7.2	7.2	7.2	7.2
Decomposition of CFC-11	66.4	77.1	90.8	98.2	92.7	67.4
Gas products (based on CFC-11 fed)						
CO	0.3	—	64.2	64.6	41.3	—
CO_2	0.2	—	4.1	42.3	26.6	—
$CClF_3$	3.4	7.8	0.4	0.0	3.6	0.8
CCl_2F_2	14.9	23.7	3.9	0.3	3.3	0.8
CCl_4	2.0	2.7	1.6	0.3	1.2	0.3
$C_2Cl_2F_2$	0.0	0.0	0.0	0.0	0.0	12.0
C_2Cl_3F	0.0	0.0	0.0	0.0	0.0	1.8
$C_2Cl_3F_3$	4.2	2.2	0.1	0.0	0.1	0.2
C_2Cl_4	0.1	0.1	0.0	0.1	0.1	5.4
$C_2Cl_4F_2$	3.5	5.4	1.4	0.4	0.2	0.3
Soot (carbon base)	15.9	—	7.4	2.2	1.3	16.1
Mass balance (carbon base)	85.9	—	93.8	112.5	85.4	90.0

CFC-11, 1.25 vol% : Argon flow rate, 40 L min^{-1}

Table 4

halocarbon	conc./%	H_2O/ halocarbon	conversion /%
$C_2Cl_3F_3$ [b]	0.4	6.3	100
$CHCl_3$ [c]	0.3	4.2	97
C_2HCl_3 [c]	0.2	6.3	89
CCl_4 [c]	0.6	2.1	89

a) Plate Power 10.4 kW. b) Total Flow Rate 40 L min^{-1}. c) Total Flow Rate 20 L min^{-1}.

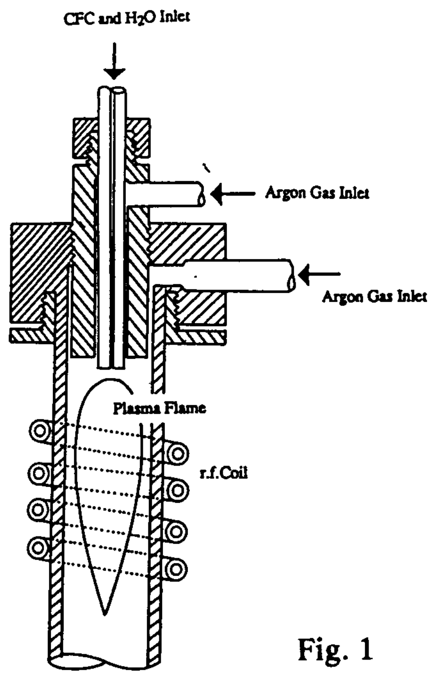

Fig. 1

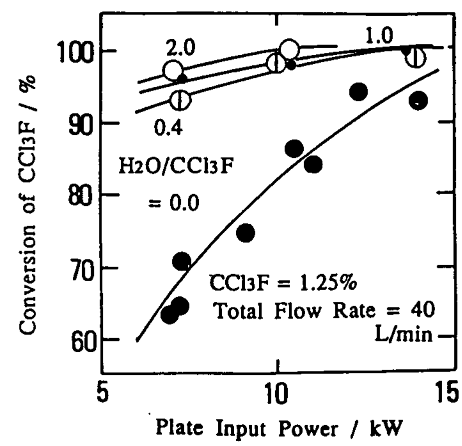

Fig. 2

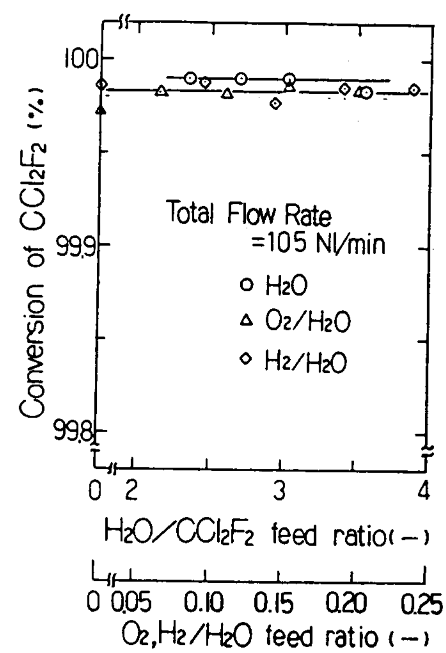

Fig. 3