Thermal Behavior of Chlorofluorocarbons (CFCs) and Formation of PCDDs/PCDFs & PFDDs/PFDFs

Sakai,S.[a*], Hiraoka,M.[b], Shiozaki,K.[c]
a)Environment Preservation Center, Kyoto Univ., Kyoto 606-01, Japan
b)Institute of Systems Engineering Research for Global Environment, Kyoto 600, Japan
c)Kaneka Techno Research Co., Ltd., Yoshida-cho, Hyogo-ku, Kobe 602, Japan

1. Introduction

Chlorofluorocarbons (CFCs) has been consumed in many fields such as refrigerants, solvents and insulating materials. "Wien Treaty for Protection of Ozone Layer" and "Montreal Protocol for Ozone Depleting Substances" were adopted to prohibit a part of CFC being used. Some CFCs have been used in various waste materials such as a coolant of refrigerators which will be emitted from waste stream over a long period of time. Therefore, the proper control method of those waste should be used. When CFCs are incinerated, by-products such as Dioxins and related compounds should be taken into a special attention[1,2]. Recently, Weber and others have synthesized PFDDs/PFDFs and established their analytical methods[3,4]. Toxicological study has shown 2,3,7,8-TFDD activates the dioxin receptor and the calculation of TCDD equivalent factor (TEF) of ca 1.0 is applicable for 2,3,7,8-TFDD. Therefore, the thermal behavior of PFDDs/PFDFs in the CFC destruction should be studied. In this paper, trichlorofluoromethane (CFC11) and dichlorodifluoromethane (CFC12) were incinerated oxidatively in the laboratory-scale atomizing combustion plant. The destruction efficiencies of these CFCs, the emission of PCDDs/PCDFs and the analytical results of PFDDs/PFDFs will be discussed.

2. EXPERIMENTAL METHODS

A schematic flow of the laboratory-scale plant is shown in Figure 1. It consists of an atomizing combustion chamber, a quenching tank, a gas cooler and a scrubbing tower. The capacity of this plant is about 20,000 kcal/hr. Liquid waste is supplied from the top of incinerator and decomposed with liquefied petroleum gas (LPG). CFC12 is supplied into an incinerator with LPG in the gas supply line. Combustion gases are cooled rapidly in a quenching tank and a gas cooler. Acid gases such as HCl and HF are neutralized in a scrubbing tower with sodium hydroxide. CFC11 is supplied as liquid state with toluene containing carbontetrachloride and dichloromethane. CFC11, carbontetrachloride and

dichloromethane had approximately 3 percent of total liquid waste and CFC12 was 5 to 10 % of LPG as weight percent.

The analytical method of PFDDs/PFDFs was based on the study by Weber and others[3]. The HRGC/HRMS was HP5890 SERIES Ⅱ and VG Autospec operating at a resolution of about 10,000. GC column for PFDDs/PFDFs was CP-Sil 88 fused silica column, 50m × 0.25 mm i.d., film thickness of 0.2 μ m. Column heating condition was the same as Weber and as follows: 90 °C; 2.7 °C/min to 150 °C, 4 min isothermal; 8 °C/min to 170 °C, 3 min isothermal; 20 °C/min to 245 °C, 10 min isothermal. For quantitative analyses the mass spectrometer was run in the SIM mode. Mass monitoring ions used were for M_1FDD, 202.0430, D_2FDD; 220.0336, T_3FDD; 238.0242, T_4FDD; 256.0147, P_5FDD; 274.0053, H_6FDD; 291.9959, H_7FDD; 309.9865, O_8FDD; 327.9771, M_1FDF; 186.0481, D_2FDF; 204.0387, T_3FDF; 222.0292, T_4FDF; 240.0198, P_5FDF;258.0104, H_6FDF; 276.0010, H_7FDF; 293.9916, O_8FDF; 311.9821. Identification of each peak was based on the standard mixture and its chromatogram supplied by Prof. Hagenmaier.

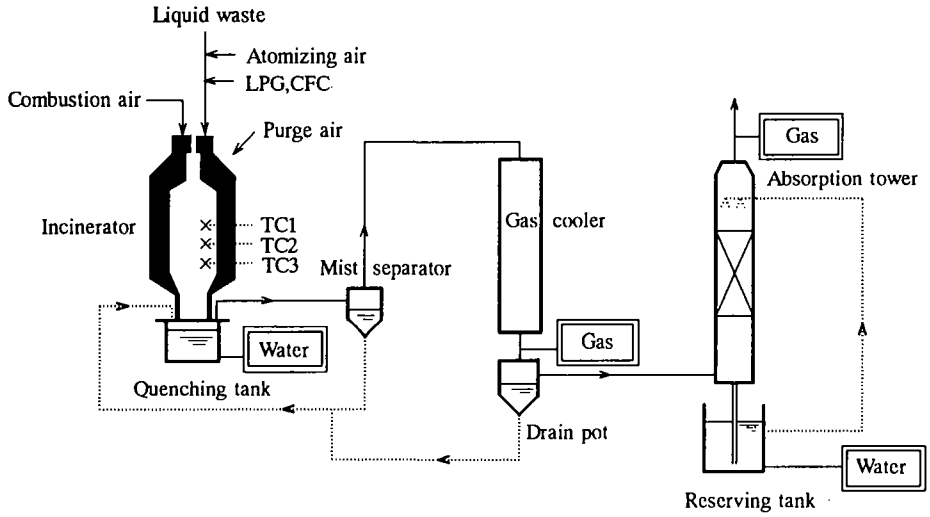

Figure 1 Flow diagram of laboratory-scale incineration plant

3. RESULTS AND DISCUSSION

Destruction efficiency and CFCs' concentration are shown in Table 1. No CFC11 were detected (< 10 $\mu g/Nm^3$) both in the outlet of gas cooler and the outlet of alkaline absorber. Only low temperature of 740 °C had the detection of CFC11, 89 and 77 $\mu g/Nm^3$, with the presence of dichloromethane. The destruction efficiency (DRE) of CFC11 are more than 99.999 % (5 nine) in all conditions. CFC12 has the DRE of more than 5 nine in the temperature of 1070 °C and 970 °C. Lower temperature of 740 °C, however, shows the DRE of 4 nine. CFCs were not detected in the quenching water and the scrubbing water (< 5 $\mu g/L$). Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were in the order of 0.01 ng TEQ/ Nm^3 or less in three conditions as shown in Table 2. Total PCDDs/PCDFs of 740 °C was 61 ng/ Nm^3, although the temperature of 970 °C and 1070 °C showed 0.94 ng/ Nm^3 and 1.6 ng/ Nm^3 of the total PCDDs/PCDFs.

Table 1 Destruction efficiency of CFCs and other halogenated compounds

	Temp.	Outlet of Gas Cooler			Outlet of Alkaline Scrubber		
		Conc.	Mass Flow	Destruction Efficiency	Conc.	Mass Flow	Destruction Efficiency
	[°C]	[$\mu g/Nm^3$]	[mg/h]	[%]	[$\mu g/Nm^3$]	[mg/h]	[%]
Dichloromethane							
RUN 27	1070	<10	<0.28	>99.99915	<10	<0.28	>99.99915
RUN 28	970	<10	<0.23	>99.99921	<10	<0.23	>99.99921
RUN 29	740	14	0.16	99.9989	34	0.38	99.99973
Carbon Tetrachloride							
RUN 27	1070	<15	<0.42	>99.9987	<15	<0.42	>99.9987
RUN 28	970	<15	<0.34	>99.9989	<15	<0.34	>99.9989
RUN 29	740	<15	<0.17	>99.9988	<15	<0.17	>99.9988
CFC11							
RUN 27	1070	<10	<0.28	>99.99907	<10	<0.28	>99.99907
RUN 28	970	<10	<0.23	>99.99926	<10	<0.23	>99.99926
RUN 29	740	<10	<0.11	>99.99927	<10	<0.11	>99.99927
CFC12							
RUN 27	1070	<10	<0.28	>99.99959	24	0.66	99.99903
RUN 28	970	<10	<0.23	>99.99943	<10	<0.23	>99.99943
RUN 29	740	89	1.0	99.9941	77	0.86	99.9949

Table 2 PCDDs/PCDFs in the oxidative conditions of CFCs destruction

	RUN 27	RUN 28	RUN 29
Temperature [°C]	1070	970	740
O_2 Concentration [%]	6.7	7.6	7.4
Waste Composition	Mixture*1	Mixture*1	Mixture*1
CFC12 Loading [weight % to LPG]	9.1	7.5	5.9
T_4CDDs	0.19	0.05	1.7
P_5CDDs	0.05	< 0.01	0.19
H_6CDDs	0.02	0.01	0.22
H_7CDDs	0.12	0.04	0.20
O_8CDD	0.28	0.05	0.42
Total PCDDs (TEQ)*2	0.66(0.004)	0.15(0.000)	2.7(0.010)
T_4CDFs	0.34	0.63	56
P_5CDFs	0.08	0.01	0.79
H_6CDFs	0.05	< 0.01	0.15
H_7CDFs	0.23	0.08	0.21
O_8CDF	0.23	0.06	0.24
Total PCDFs (TEQ)	0.93(0.009)	0.79(0.000)	58(0.017)
Total PCDDs/PCDFs (TEQ)	1.6(0.013)	0.94(0.000)	61(0.027)
2,3,7,8-T_4CDD	< 0.01	< 0.01	< 0.01

*1: CFC11; 2.5~3.38%, carbontetrachloride; 2.71~3.38%, dichloromethane; 2.79~3.36%

*2: 2,3,7,8-TCDD toxicity equivalent concentration [ng TEQ/ Nm^3 @ O_2=12%]

Table 3 PFDDs/PFDFs in the oxidative conditions of CFCs destruction

	RUN 27	RUN 28	RUN 29
Temperature [°C]	1070	970	740
O_2 Concentration [%]	6.7	7.6	7.4
Waste Composition	Mixture*1	Mixture*1	Mixture*1
CFC12 Loading [weight % to LPG]	9.1	7.5	5.9
M_1FDDs	0.08	0.17	0.12
D_2FDDs	0.30	0.19	0.21
T_3FDDs	0.36	0.22	0.27
T_4FDDs	0.59	0.16	0.39
P_5FDDs	< 0.01	< 0.01	< 0.01
H_6FDDs	0.63	< 0.01	0.45
H_7FDDs	< 0.01	< 0.01	< 0.01
O_8FDD	0.14	0.30	0.21
Total PFDDs [ng/ Nm^3]	2.1	1.0	1.6
M_1FDFs	< 0.01	0.19	< 0.01
D_2FDFs	0.08	0.05	< 0.01
T_3FDFs	< 0.01	< 0.01	< 0.01
T_4FDFs	< 0.01	< 0.01	< 0.01
P_5FDFs	< 0.01	< 0.01	< 0.01
H_6FDFs	< 0.01	< 0.01	< 0.01
H_7FDFs	< 0.01	< 0.01	< 0.01
O_8FDF	< 0.01	< 0.01	< 0.01
Total PFDFs [ng/ Nm^3]	0.08	0.24	< 0.01
Total PFDDs/PFDFs [ng/ Nm^3]	2.2	1.2	1.6
2,3,7,8-T_4FDD [ng/ Nm^3]	0.10	0.07	0.09

*1: CFC11; 2.5~3.38%, carbontetrachloride; 2.71~3.38%, dichloromethane; 2.79~3.36%

PFDDs/PFDFs were detected in all three oxidative conditions of CFCs destruction (Table 3). Total concentration of $M_1FDD/M_1FDF \sim O_8FDD/O_8FDF$ were 2.2, 1.2, 1.6 ng/ Nm^3 for 1070 °C, 970 °C and 740 °C respectively. 2,3,7,8-TFDD were 0.10, 0.07, 0.09 ng/ Nm^3, which are higher than 2,3,7,8-TCDD (< 0.01 ng/ Nm^3). According to the pyrolysis experiment of CFC11 by Weber et. al. [3], PFDDs/PFDFs could not be detected during a pyrolysis treatment of CFC11 or Teflon. They reported no PFDDs/PFDFs could be detected for a number of MWI fly ash samples with detection limits in the range of 0.01 ng/g for individual components. Our limited analysis also shows no detection of PFDDs/PFDFs for MWI fly ash. However, CFC destruction in oxidative condition shows a small amount of PFDDs/PFDFs formation. Toxicological evaluation of these detection is necessary based on the further information of toxicological equivalent factor.

ACKNOWLEDGMENTS

The authors would like to thank Professor Hagenmaier (University of Tübingen) for the supply of PFDDs/PFDFs standard.

REFERENCES

1 Rittmeyer,C. and Vehlow,J. (1993): Decomposition of Organohalogen Compounds in Municipal Solid Waste Incineration Plants. Part 1: Chlrofluorocarbons, Chemosphere, 26, 2129-2138.

2 Hall,R., Lee,C., Hassel,G., Ryan,J. (1991): Experimental Investigation of PIC Formation in CFC Incineration, EPA/600/A-92/021.

3 Weber,R., Schrenk,D., Schmitz,H.J., Hagenmaier,A. and Hagenmaier,H. (1994): Polyfluorinated Dibenzodioxins and Dibenzofurans- Synthesis, Analysis, Formation and Toxicology, Chemosphere, 30, 629-639.

4 Haffer,U., Rotard,W. and Mailahn,W. (1994): Synthesis of Polyfluorinated Dobenzo-p-dioxins, Chemosphere, 29, 1803-1809.