Development of CFCs Decomposition System Using Microwave Plasma

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Chlorofluorocarbons, CFCs, long used as refrigerants in air conditioners and refrigerators have been found to contribute to the destruction of the earth's ozone layer. We decomposed CFCs by microwave-discharged thermal plasma under atmospheric pressure. The plasma consisted only of CFCs and steam, resulting in low gas emission and high electrical efficiency because no other gas such as Ar, He, LNG, or LPG is needed in this process to break down over 99.99% of CFCs. Gas discharge after neutralization met United Nations Environment Programme (UNEP) guidelines and dioxin in the emitted gas was much less than the regulation set in Japan.

1. Introduction

Chlorofluorocarbons (CFCs) long used as detergents, refrigerants, foaming agents, propellants, etc. have been found to destroy ozone layer and cause global warming when released to the atmosphere. Their emission therefore has currently come to be prohibited in global scale(1). Consequently, the development of alternative technologies (substitutes and alternating process) to these ozone depleting Substances (ODS) together with the establishment of emission control technologies such as recovery and decomposition has become an imminent demand. At present there are two methods for treating the recovered CFCs: ① large-scale centralized treating and ② small-scale distributed treating through decomposition. As for the decomposition of CFCs, various methods have been studied, developed and partly put into practical use such as burning method(2), catalytic method, plasma method(3) (4), detonation method, etc. In our development project we used thermal plasma method, which ensures steady decomposition and enables miniaturization of the decomposition unit, with a view to realizing a small-scale distributed treating type CFCs decomposition unit. Further, we selected the microwave plasma method, and evaluated the decomposition performance and studied the harmless treatment of waste gas in order to develop a compact distributed CFCs decomposition system.

2. Tho present status of CFCs decomposition

The CFCs from refrigerators, car air conditioners, and refrigerator and air conditioners for business use are refilled mainly in 20-kg cylinders using CFCs recovery system, and in case of large-scale centralized treating, 10 to 20 such cylinders are stored before being transported to the facilities for decomposition. In this case, however, because of the transportation cost and the need of possessing and storing a large number of cylinders before the return of cylinders, there is a high demand of distributed treating system to allow handy and simple treatment. In the case of distributed treating, the recovered CFCs from a factory can be treated inside the factory, contributing to the reduction in decomposition cost.

In Japan more than 30 CFCs decomposition facilities including the small-scale ones with feed rate 1 kg/h and the large-scale ones with feed rate 140 kg/h are in operation, with the treating capacity estimated to be approximately 3 000 t/y.

3. CFCs decomposition system using microwave plasma system

3.1 Target of development

In the process of development of CFCs decomposition system using microwave plasma, we started by setting the target values for CFCs feed rate, CFCs decomposition rate, and feed rate per unit power as shown in **Table 1**. The CFCs feed rate was set to 2 kg/h in view of the market survey and product data obtained previously through hearing, etc. Further, the CFCs decomposition rate was based on the value recommended by UNEP (United Nations Environment Programme) and the feed rate per unit power to ensure performance higher than in other plasma systems. In order to achieve the target values of feed rate and decomposition rate, elementary tests were conducted to study the required microwave power. Further, in order to achieve the high CFC 12 feed rate per unit power, the optimum design of cavity through electromagnetic analysis and the Argonless plasma generating technology needing no carrier gas were studied and adopted.

3.2 Generation of microwave plasma

Microwave generally refers to the electromagnetic wave with the frequency ranging from 1 GHz to several hundred GHz. In this decomposition system, however, we used the microwave of 2.45 GHz to generate plasma.

Fig. 1 shows the microwave plasma generating circuit. The microwave, generated from the magnetron furnished in the microwave oscillator, is fed into MHI's coaxial cavity with unique structure through the isolator, waveguide, and coaxial waveguide converter. The introduced microwave creates a high electric field in the gap between the inside axle (probe antenna) and the end plate inside the coaxial cavity shown in **Fig. 2** by means of the TM_{010} mode that generates an electric field in the axial direction of the resonator. The cavity is equipped coaxially inside with a discharge tube, inside which

Table 1 Development goals

Item	Target
Feed rate (CFC 12)	2 kg/h
CFCs decomposition rate	99.99% or over
Feed rate per unit power	0.5 kg/kWh or over
Waste gas component	UNEP guideline value
HCl	< 100 mg/m³
HF	< 5 mg/m³
CO	< 100 mg/m³

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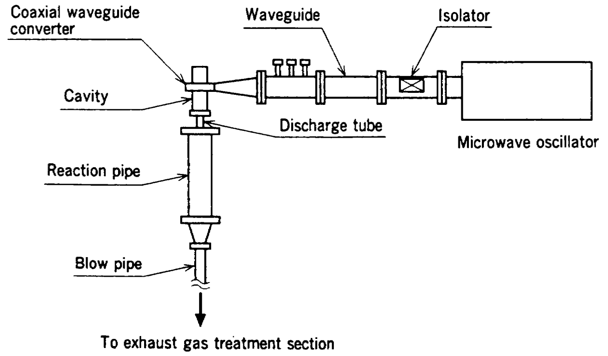

Fig. 1 Microwave plasma generating circuit
Three-dimensional circuit for generating microwave plasma used in the CFCs decomposition system is shown.

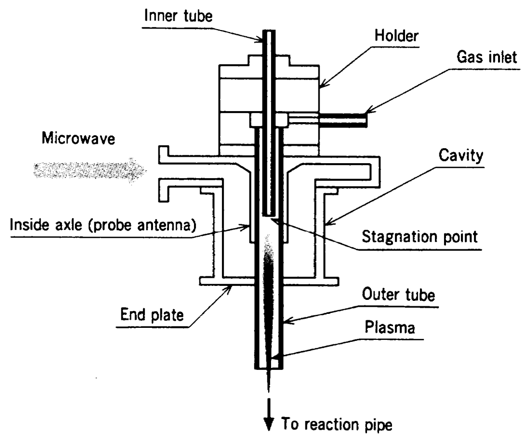

Fig. 2 Structure of cavity and discharged section
The detailed structure of the microwave plasma generating section composed of the cavity and the discharge tube is shown.

plasma is generated. The discharge tube is composed of an inner tube, an outer tube, and a metallic holder to hold them. The inner and outer tubes are designed to have optimum sizes befitting with the gas flow rate, so as not cause melting fracture, etc. due to plasma heat. Further, the holder has a hole between the outer and inner tubes to allow the gas supplied from the gas inlet to flow. The double-tube action of these inner and outer tubes helps form a stagnation point at the end of the inner tube to enable easy retaining of plasma and to prevent plasma flame from getting unsteady.

3.3 System configuration

Fig. 3 shows the system flow of CFCs decomposition system. The system can be broadly divided into three components: gas supply section, plasma generating section, decomposition reaction section, and exhaust gas treatment section.

When water vapor is used as the process gas, the decomposition reaction of CFC 12 can be expressed by equation (1).

$$CCl_2F_2 + 2\,H_2O \rightarrow 2\,HCl + 2\,HF + CO_2 \qquad (1)$$

CFC 12 reacts with water to get decomposed into hydrogen chloride, hydrogen fluoride, and carbon dioxide.

In Fig. 3, the CFCs supplied from the cylinder and the water fed from the metering pump get heated up to approx. 150°C in a water vapor generator equipped with an electric heater to become a mixture of CFCs/water vapor (steam) before being supplied to the plasma generating section. The Ar in Fig. 3 is used only at the time of plasma ignition, and is not used as a process gas during operation. The mixture of CFCs/water vapor supplied to the plasma generating section receives the plasma effect due to the microwave and turns into dissociated state. The substances under dissociated state react with one another in the reaction pipe connected to the downstream side to keep the chemical equilibrium before turning into hydrogen chloride, hydrogen fluoride, and carbon dioxide. In order to neutralize the two strong-acid gasses, hydrogen chloride and hydrogen fluoride, the bubbling tower method using slaked lime slurry was selected because of the reasons given below.

(1) The method is suitable for the neutralization of a gas with high velocity of dissolution in water.

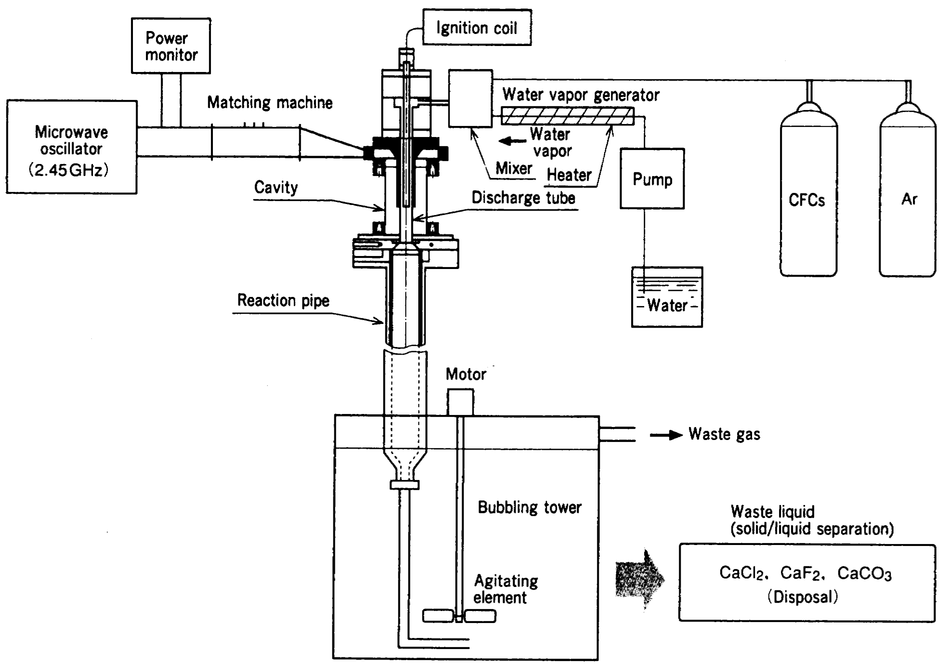

Fig. 3 Apparatus of CFCs decomposition system
The outline of the CFCs decomposition system used in the test is shown.

(2) The method is easily applicable to the case with little waste gas.

(3) The equipment can be made compact and less costly.

The neutralization reaction between slaked lime and hydrogen chloride or hydrogen fluoride is expressed by equation (2).

$$2\,HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2\,H_2O$$
$$2\,HF + Ca(OH)_2 \rightarrow CaF_2 + 2\,H_2O \qquad (2)$$

Calcium chloride in the equation dissolves in water, while calcium fluoride, with low solubility, remains in the liquid in solid state.

3.4 Features of microwave plasma method

The CFCs decomposition system using microwave plasma has the features given below.

① Since the decomposition takes place in a very high temperature field (approx. 6 000 K), the decomposition can be completed in shorter time than in the other method. This ensures steady decomposition efficiency, and since the design residence time is short, the decomposition reaction section can be miniaturized.

② Since the required very-high temperature field can be created instantaneously by turning the power to ON, the system can be started up in a short time, ensuring outstanding operability.

③ Water vapor can be used as a process gas and a high decomposition rate is obtainable through the action (effect) of OH radical.

④ Since there is no need of assertive gasses such as Ar, LNG, LPG, etc., the method has high power efficiency and is less costly. Further, since the amount of exhaust gas is small, the exhaust gas processor can be made compact in size.

4. CFCs decomposition performance

4.1 Decomposition of special CFC (CFC 12)

The decomposition verification test of special CFC (CFC 12) was carried out by using the CFCs decomposition system shown in Fig. 3.

From the aforesaid decomposition reaction equation (1) of CFC 12, the stoichiometric quantity of H_2O needed for decomposition of 1 mole CFC 12 is 2 mole. However, when decomposed using the stoichiometric ratio, even a slight inadequacy of the mixture of CFC and water vapor easily causes imperfect oxidation, producing CO. Hence, we carried out the decomposition test by supplying H_2O 1.5 times larger in quantity than the stoichiometric ratio. The experimental conditions for CFC 12 are given in **Table 2**.

Further specifications of CFCs decomposition system are summed up in **Table 3**.

Fig. 4 shows the variation in decomposition rate when the applied microwave power is changed, with the CFC 12 feed rate kept constant at 2.0 kg/h. The decomposition rate at 1.8 kW microwave power has been confirmed to clear the decomposition rate of 99.99% recommended by UNEP (United Nations Environment Programme). It has further been confirmed that the discharge pipeshows no melting fracture up to the microwave power of 2.4 kW, ensuring steady decomposition operation. The cause of the decomposition rate getting affected by the microwave power is considered to be the change in decomposition field zone and temperature.

Fig. 5 shows the measured decomposition rate of CFC 12 when the CFC 12 feed rate is changed.

At microwave power 2.0 kW, no peak of CFC 12 or undecomposed residue is observed in the exhaust gas within the range of CFC 12 feed rate 1.0 to 2.1 kg/h, and the decomposition rate is as high as 99.99% or over. However, at the feed rate 2.3 kg/h, the decomposition rate gets decreased (99.957%), falling short of the expected performance. The decomposition rate was found to decrease at the feed rate 2.0 kg/h at microwave power 1.5 kW and at the feed rate 1.5 kg/h at microwave power 1.25 kW. No decline was seen in the decomposition rate to the extent the feed rate was 2.3 kg/h at microwave power 2.3 kW. **Fig. 6** shows the test result in terms of the relationship between CFC 12 feed rate per unit electric power and decomposition rate.

The decomposition rate clears the target value up to the range of the feed rate per unit electric power=1.0 kg/kWh, beyond which the decomposition rate shows a decline.

Table 2 Experimental conditions

Applied microwave power	1.25—2.3 kW
CFC 12 feed rate	1.0—2.3 kg/h
Molar ratio between water vapor and CFC 12	3.0
Air flow rate for combustion	0.6—1.8 Nm³/h
Slaked lime concentration	10 wt%
Rotational frequency of neutralization tank for stirring	360 rpm

Table 3 Specification of CFCs decomposition system

Destruction method	Microwave plasma method
Decomposition rate	99.99% or over
Microwave frequency	2.45 GHz
CFCs for destruction	CFC 12, HCFC 22, HFC 134 a, R-502, etc.
Feed CFCs concentration	23—33 vol%
Process gas	Water (water vapor), air, Ar (only at start)
Decomposition temperature	6 000 K or over
Pressure	1.0—1.2 kg/cm²
Gas residence time	0.5—1.0 s
Decomposed-gas treating method	Neutralization due to bubbling tower (slaked lime slurry)
Exhaust gas temperature	20—70 °C
Utilities	Water, air, Ar, electricity, and slaked lime
Power consumption	5.5 kW

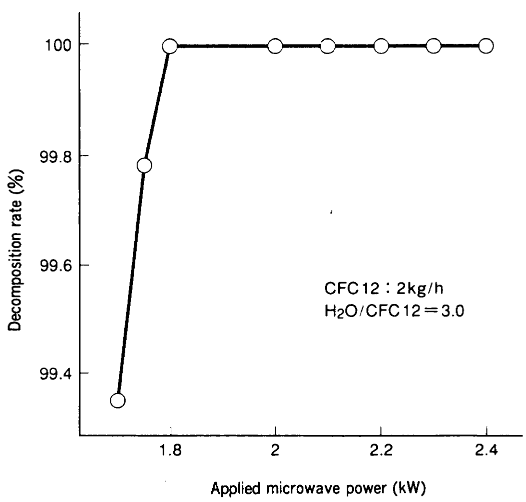

Fig. 4 Relationship between CFCs decomposition rate and microwave power.
High decomposition rate is confirmed at microwave power 1.8 kW or over.

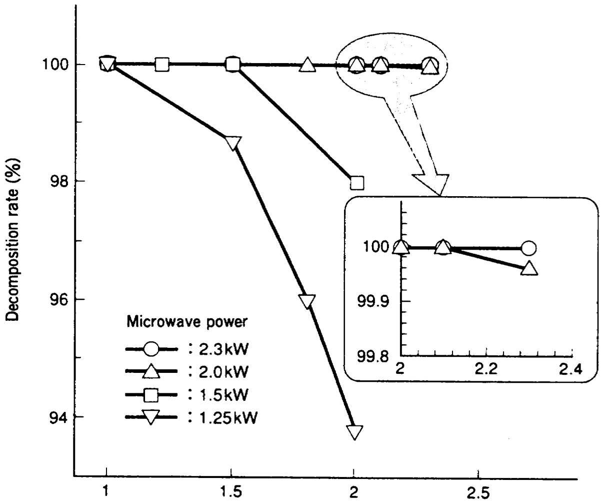

Fig. 5 Relationship between CFC12 decomposition rate and feed rate
High decomposition rate is confirmed at CFC 12 feed rate up to 1.7–2.1 kg/h.

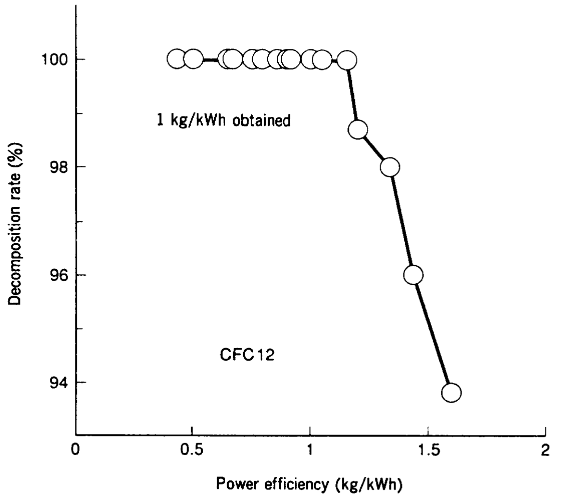

Fig. 6 Relationship between CFC12 feed rate per electric power and decomposition rate
Decomposition rate of 99.99% or over is confirmed at CFCs feed rate per unit electric power: 1 kg/kWh, beyond which the decomposition rate got decreased.

Consequently, the microwave power needed to obtain the target feed rate 2 kg/h is 1.8 kW or over from Fig. 4. For safety's sake, if the microwave power is 2.0 kW, the feed rate per unit electric power comes to be 1.0 kg/kWh, clearing our target value.

4.2 Properties of decomposed exhaust gas

Table 4 shows the analytical data of the exhaust gas after neutralization together with the guideline values of UNEP. In the exhaust gas no peak is observed attributing to CFC 12 or undecomposed residues. O_2 and N_2 in Table 4 are produced by the combustion air added at the plasma downstream in order to accelerate the conversion of CO into CO_2. The result of analysis has therefore clearly indicated that the hydrochloride and hydrofluoride produced after decomposition are below the detectable limit and have substantially been converted into innocent substances in the neutralization tank. Further, the analytical data have cleared all the guideline values of UNEP. The performance of the newly developed CFCs decomposition system has therefore been theoretically proved. The density (concentration) of DXNs was also measured and was found to be below the recommended level.

Besides, we also carried out test on HCFC 22 and HFC 134 a only to find the excellent results equivalent to CFC 12.

5. Future prospect

Our initial goal of development has been accomplished through the result of test using the principle verification machine. We are planning to carry out further long-term endurance tests in the future to confirm the durability of magnetron, discharge pipe etc., corrosion resistance, life, etc. of materials. The newly developed decomposition system has been successfully built into a compact size: width 1.79 × depth 1.14 × height 1.95 m, and has already been launched in the market.

As for the calcium fluoride, etc. contained in the waste liquid after neutralization, it is necessary to continue study to find an effective utilization method instead of disposing them simply as industrial wastes.

We are also planning to widen the application of the technique for converting toxic substance into innocent substance by using microwave plasma. We are making study on the effectiveness of this process also in other substances causing global warming, such as PFC (Perfluorocarbon) used in the production of semiconductors in addition to the other CFCs viz. CFC, HCFC, and HFC.

6. Conclusion

The principle verification test using microwave plasma was carried out with an object of converting special CFCs, a substance affecting the global environment, into innocent substance to make the following points clear.

(1) The mixture of CFCs and water vapor was successfully turned into plasma by using microwave, and a high-efficiency and low-cost treating process needing no assist (assertive) gas was established.

(2) In decomposition of CFC 12, the feed rate of 2 kg/h could be obtained at microwave electric power of 2 kW, with the

Table 4 Analysis data of composition of exhaust gas at CFC 12 decomposed

Substance name	Measured value	UNEP guideline value
CFC 12 density	0.5ppm	Decomposition rate:99.99% or over
HCl (Hydrogen chloride) density	<0.3 mg/Nm³	<100 mg/Nm³
HF (Hydrogen fluoride) density	<0.7 mg/Nm³	<5 mg/Nm³
CO (Carbon monoxide) density	4 mg/Nm³	<100 mg/Nm³
DXNs	0.001 ng-TEQ/Nm³	<1.0 ng-TEQ/Nm³
O_2 (Oxygen) density	11.6 vol%	–
N_2 (Nitrogen) density	87.2 vol%	–
CO_2 (Carbon dioxide) density	1.1 vol%	–
Cl_2 (Chlorine) density	<2.0 mg/Nm³	–

decomposition rate clearing the target value at 99.99% or over.

(3) The toxic substances contained in the decomposed gas such as hydrochloride and hydrofluoride were thoroughly neutralized and eliminated by means of bubbling tower, and these substances were not contained in the exhaust gas. Further, the carbon monoxide content in the exhaust gas was also found to clear the control value.

We are determined to confirm the durability of the system through the long-term endurance test and to widen the application of the new technology to decomposition of the other toxic substances.

References

(1) Hiraoka, M., Control of Ozone Depleting Substances (ODS) and Trends in Recovery, Recycling and Destruction of ODS, Journal of the Japan Society of Waste Management Experts Vol.5 No.4 (1994) p.344

(2) Urano, K. et al., Destruction of CFCs Using Incinerator of Industrial Waste, The 5th Annual Conference of the Japan Society of Waste Management Experts (1994) p.501

(3) Mizuno, K., The Measures against Destruction of Ozone Depleting, Journal of the Japan Society of Atmospheric Environment Vol.31 No.4 (1996) p.83

(4) Mizuno, K. et al., Inductively Coupled r. f. Plasma Reactor for Destruction of Ozone Depleting Substances, Thermal Science and Engineering Vol.3 No.3 (1995) p.141