The First Step to Industrialize Decomposition Process of Ozone Depleting Substances by Steam Plasma

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ABSTRACT

A novel process to decompose ozone depleting substances (ODS) has been developed. In this process, ODS fed into a 100% steam plasma are completely decomposed and converted to the product gases, comprised of CO_2 and hydrogen halides, which are quenched and neutralized in a scrubber to yield calcium halides, and are separated by sedimentation. The conversion efficiency has been achieved up to more than 99.99 %. The throughput rate for CFC-12 and halon-1301 has been more than 50 kg/h by r.f. generator of 180 kW at the plate power level. The analysis of the exhaust gases has indicated that hydrogen halides are completely removed in the quenching tank and scrubber.

Thermodynamic calculation revealed that the induction input of 90 kW (a half of the plate power) corresponds to the average gas temperature of 3,030 K and the power input needed in this process is considered to be much smaller than the anticipated value. The experimental electric power consumption value of 4 kWh/kg is industrially acceptable.

INTRODUCTION

The depletion of the stratospheric ozone layer is known to arise from the chlorofluorocarbons (CFC), halons and several kinds of chlorinated hydrocarbons released into the atmosphere. In addition, it is also estimated that the contribution of CFC to the global warming is 24 %, which is second to that of 55 % due to carbon dioxide[1]. The authors has been developing the decomposition process of ODS by an induction steam plasma[2,3]. Thermodynamic analysis has predicted that the input steam/ODS ratio should be higher than 2 for CFC-12 (CCl_2F_2). When the ratio is 2, the overall reaction is written as Eq.(1).

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

Thermodynamic analysis has been also useful to discuss the energy efficiency of the plant. The concept of normalized minimum plate power : $Pmin/\Delta H(10{,}000)$ (where Pmin and $\Delta H(10{,}000)$ are defined by Eq.(4) and Eq.(2), respectively) has been introduced. It is the ratio of the experimental energy to the theoritical one.

$$\Delta H(T) = \left(\sum_{i(product)} N_i(T) \cdot H_i(T) - \sum_{j(raw)} N_j \cdot H_j\right) \Big/ \sum_{j(raw)} N_j \qquad \text{(kJ/mole)} \qquad (2)$$

where N_i : mole number of i species (mole)

H_i : mole enthalpy of i species (kJ/mole)

$$\Delta H(10{,}000) \doteqdot 236 \cdot n_{Ar} + 1637 \cdot n_{H2O} + 2887 \cdot n_{CCl3F} + 2998 \cdot n_{CCl2F2} + 984 n \cdot_{O2} + 903 \cdot n_{H2} \qquad \text{(kJ/mole)} \qquad (3)$$

where n_i : mole fraction of i species

$$Pmin = Wmin / \sum_{j(raw)} Q_j \qquad \text{(kJ/mole)} \qquad (4)$$

where Wmin : minimum plate power (kW)

Q_j : incoming rate of j species (mole/s)

In the course of scaling up the plant, the maximum plate power of r.f. generator has been increased from 30, 70 to 180 kW. The normalized minimum plate power were found to be about 0.3 in Ar-steam system for all plant. The existence of optimum total gas flow rates to reduce the normalized minimum plate power were also found. They were around 80, 100, and 400 Nl/min, respectively. The plate power of 180 kW was found to be sufficient for generating pure and stable steam plasma.

This paper presents the details of 180 kW pilot plant and the experimental results of the decomposition of CFC-12 and halon-1301 ($CBrF_3$). The energy analysis of the process is also presented with thermodynamic consideration.

EXPERIMENTAL METHOD

The entire pilot plant system is comprised of ODS and steam feeders, a plasma generator connected to a plasma torch, a reaction chamber, a cooling chamber, a gas scrubber, a vacuum pump, an activated carbon tank, and a waste water treatment unit. Figure 1 shows a schematic of the 180 kW pilot plant of ODS decomposition process. It is roughly divided into the following two parts. One is a plasma pyro-hydrolysis system in which ODS and steam are rapidly heated to plasma temperature using induction r.f. plasma, decomposed, and then recombine in the reaction chamber. The other is a waste-gas flash-cooling system in which exhaust gas at high temperature is quenched to a level below 80 °C to prevent decomposed gas from recombining to form dioxins (Polychloro Dibenzo p-Dioxins (PCDD) and Polychloro Dibenzo Furans (PCDF)).

Raw materials are evaporated by heaters in ODS and steam feeders. The feeding line is heated to prevent them from condensing. The induction plasma torch has a plasma confining Si_3N_4 tube of 61 mm inner diameter, a 3 turn coil, and a bulk head gas injector which feed all the raw material spirally along the wall of the confining tube as a sheath gas. The r.f. generator of 180 kW in plate power supplies 3.91 MHz r.f. current. Since the maximum temperature in the plasma torch is said to be about 10,000 K, the fed materials are expected to decompose completely to atomic species such as C, Cl, F, H, and O. The exit gases from the plasma torch are cooled in the reaction chamber, of which wall temperature is around 800 °C. The decomposed gases are expected to recombine to multiatomic species such as CO_2, HCl, and HF.

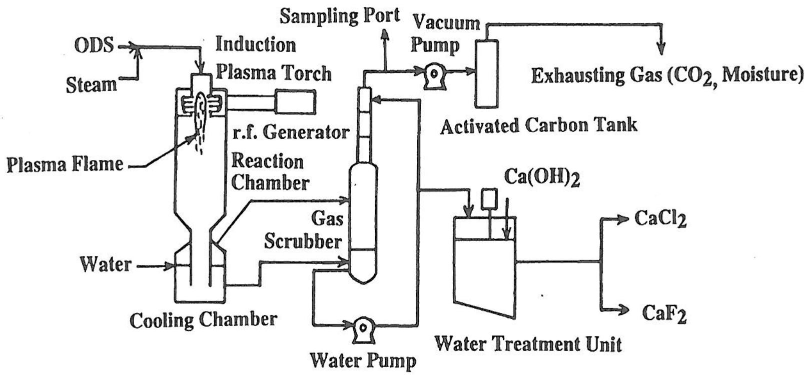

Fig. 1 Schematic of ODS decomposition pilot plant.

The decomposed waste gases are flash-cooled to about 80 °C by passing them underwater in the cooling chamber in order to minimize the residence time at around 300 °C where PCDD/PCDF tend to form. This waste gas quenching system is the same as that adopted in the high-temperature thermal decomposition plant for polychlorinated biphenyls (PCB), which has the only operating record of this kind in Japan. The acids in decomposed gas are first removed in the cooling chamber and additionally removed by absorption through counter-current contact with water in the subsequent gas scrubber. The resulting acid solution is partially extracted from the gas scrubber as a waste water. Since the waste water extracted from the gas scrubber contains harmful fluoride ions, they are allowed to react with calcium hydroxide to fix fluoride as calcium fluoride. The solution is discharged after the calcium fluoride has been separated by sedimentation.

In order to check whether harmful gas is exhausted, a gas chromatograph (GC) is equipped after the gas scrubber. GC is also used to determine the conversion efficiency (η). Although the feeding rate of ODS (Q_F) and the concentration of it at the sampling position (C_{ODS}) can be measured, total gas flow rate at the sampling position (Q_{STotal}) can not be measured directly. Therefore the calibration gas, in this case nitrogen in air, is fed to the reaction chamber simultaneously. As the feeding rate of the calibration gas is known and is not changed at the sampling position, Q_{STotal} can be calculated from the concentration of the calibration gas at the sampling position. As the out gas flow rate of ODS (Q_S) is $Q_{STotal} \cdot C_{ODS}$, η is determined as $1-Q_S/Q_F$. For the measurement of CO, TCD column has been used and FID has been used for the measurement of residual CFC. In addition to GC, the concentrations of Cl_2, HCl, HF/F_2, HBr/Br_2, and dust in the exhausting gas are analyzed.

Experimental procedure is as follows. First all the system is evacuated to the pressure of the humidity, Ar is fed, and the induction plasma is ignited. With raising the r.f. power, Ar is changed to steam, and pure steam plasma is obtained. Then the feed of ODS is started. All the experiments are carried out under 200 Torr.

EXPERIMENTAL RESULTS

Figure 2 shows an example of the operation timing chart of CFC-12 decomposition. The maximum feeding rate of CFC-12 is 50.4 kg/h. During this experiment 11 GC measurements have been made. The observed residual CFC-12 is 15 ppm at maximum. The conversion efficiency is 99.9982 % at worst. The efficiency at maximum throughput rate is 99.9995 %. Furthermore CO has not been detected in all GC measurements. Table 1 shows the results of the exhausting gas analysis. All the concentrations of the examined species are under the guideline of UNEP[4].

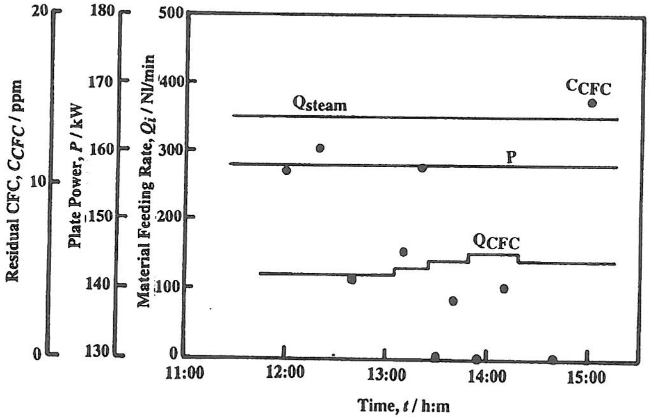

Fig. 2 Operation timing chart of CFC-12 decomposition process.

Figure 3 shows an example of the operation timing chart of halon-1301 decomposition. The maximum feeding rate of halon-1301 is 53.6 kg/h. During this experiment 20 GC measurements have been made. The observed residual halon-1301 is 6.5 ppm at maximum. The conversion efficiency is 99.9956 % at worst. The efficiency at maximum throughput rate is 99.9992 %. Furthermore CO has not been detected in all GC measurements. The results of the exhausting gas

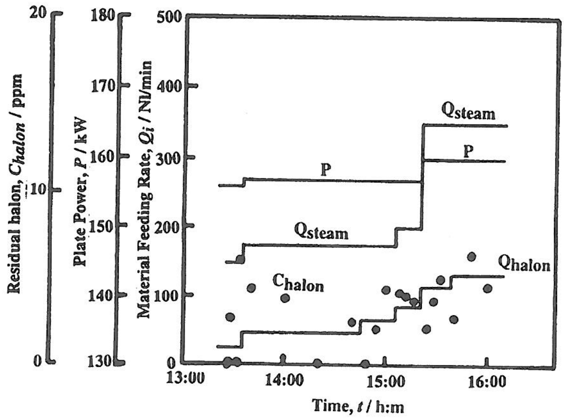

Fig. 3 Operation timing chart of halon-1301 decomposition process.

analysis are also shown in Table 1. Though the concentration of HF is over the guideline of UNEP, it is considered to be due to low capacity of the gas scrubber.

Table 1 The concentrations of harmful gases in the exhausting gas in mg/Nm^3.

Species	CFC-12	halon-1301	UNEP guideline
Cl_2	<0.05	<0.05	not defined
HCl	40	N.D.	<100
HF	2.9	34.4	<5
HBr	N.D.	2.2	<5
Dust	<10	<10	<50
CO	N.D.	N.D.	<100

DISCUSSION

In these experiments the throughput rate of more than 50 kg/h has been obtained for both CFC-12 and halon-1301. It means that the electric power consumption is 4 kWh/kg-ODS based on the primary electricity input of 200 kW. It is quite low compared with the theoretical value anticipated from Eq.(3). The process energy in the case of CFC-12 is discussed below.

When the raw material is the mixture of 67 % steam and 33 % CFC-12, the energy to heat up all the raw material to 10,000 K (ΔH(10,000)) is derived to be 2086 kJ/total-mole from the Eq.(3). For the case that material incoming rate is 15.1 kg/h (0.233 mole/s) for steam and 50.0 kg/h (0.115 mole/s) for CFC-12, it is anticipated that the energy input rate of 724 kW is required. On the other hand, the experiments show that a plate power of 180 kW is enough to decompose CFC-12 at the incoming rate of 50 kg/h (0.115 mole/s). Assuming that the incoming rate of steam is 0.233 mole/s, the plate power for unit incoming material (P) is 517 kJ/total-mole by Eq.(4). Therefore the normalized plate power (P/ΔH(10,000)) is found to be 0.248. It is a little bit lower than 0.3, which was the normalized plate power for Ar-steam systems in 30, 70, and 180 kW plant[3]. That may be attributed to lower ionizing potential of C atom. The ionizing temperature of a C including plasma has been found to be lowered by 1,000 K compared with steam plasma[2]. Considering that the induction input to plasma is about a half of the plate power, that is 90 kW in this case, only 12 % of ΔH(10,000) is sufficient to maintain plasma stable.

As the induction input is quite lower than ΔH(10,000), it is not expected that all the fed material is heated up to the ionizing temperature of 10,000 K. Therefore the average gas temperature is meaningful. By using the thermodynamic analysis method[5] utilizing SOLGASMIX[6] with the thermodynamic date in JANAF tables[7], ΔH(T) curve shown in Fig. 4 has been derived for the case of 67 % steam and 33 % CFC-12. ΔH(10,000) is found to be 2098 kJ/mole, which is

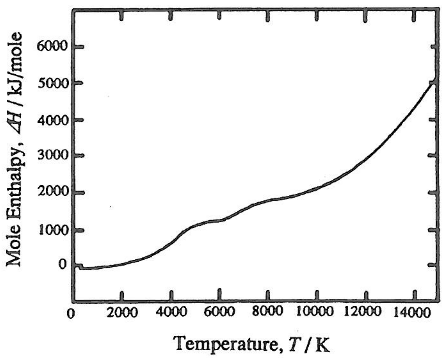

Fig. 4 The mole enthalpy (ΔH(T)) for 67 % steam and 33 % CFC-12.

almost the same as that calculated from the approximate Eq.(3). When the induction input of 90 kW and the material incoming rate of 0.233 mole/s for steam and 0.115 mole/s for CFC-12 are assumed, the energy consumption for unit incoming mole ($\Delta H(T)$) is 261 kJ/total-mole, corresponding to the average gas temperature of 3,030 K. The following two reasons may explain why the average gas temperature of 3,030 K is quite lower than the ionization temperature of 9,000 K of the C including plasma. One is that the stream temperature near the torch wall is below the destruction temperature of torch wall of about 1,300K, although the temperature of plasma skin is around 9,000 K. The other is that the mass flux of the stream near the torch wall is much higher than that in the high temperature region.

CONCLUSIONS

A pilot plant of 180 kW induction plasma is constructed to decompose ODS. From the experiments in this plant and thermodynamic consideration, following conclusions are obtained.

1. CFC-12 and halon-1301 are successfully decomposed at the throughput rate of 50 kg/h with the destruction efficiency of more than 99.99 %.
2. The harmful waste is treatable with a gas scrubber.
3. The electric power consumption is 4 kWh/kg.
4. The plate power of the process is 24 % of the theoretically determined $\Delta H(10{,}000)$.
5. The average gaseous temperature in the plasma torch is 3,030 K.

On the basis of this study, we conclude that the thermal plasma process for ODS decomposition is feasible and environmentally safe. In order to prove the stability and durability of the system, the continuous operation is under investigation on a demonstration plant, which has much exhausting gas treatment capacity, with the financial aid of NEDO (The New Energy and Industrial Technology Development Organization). The plant has been constructed in Ichikawa and is decomposing ODS collected by local governments all over Japan.

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