

# DESTRUCTION OF CH<sub>3</sub>Cl USING PLASMA FLUIDIZED CaO BED

Hidetoshi SEKIGUCHI, Naoki MATSUDERA, and Atsushi KANZAWA

Dept. Chem. Eng., Tokyo Institute of Technology  
O-okayama, Meguro-ku, Tokyo 152, JAPAN

## Abstract

A thermal plasma fluidized bed reactor was adapted to simultaneous decomposition of chloromethane and recovery of hydrogen chloride. Calcium oxide particles were used as fluidized particles. The decomposition was carried out with oxygen gas addition suggested by thermodynamic calculation. The experimental results showed the complete decomposition of CH<sub>3</sub>Cl proceeded and HCl fixation in CaO particles also took place. The bed particles also reacted with CO<sub>2</sub> and H<sub>2</sub>O. A simple model for the fluidized bed including a heterogeneous reaction between CaO and HCl was proposed to explain the recovery behavior.

## 1 Introduction

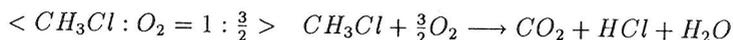
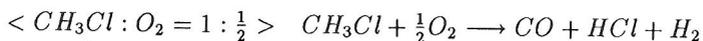
Hazardous wastes, especially halocarbons such as chlorofluorocarbons and trichloroethane, seriously affect our environment nowadays. Thus the destruction methods of these hazardous wastes must be established immediately for environmental protection. Reasonable destruction methods have to include high destruction efficiency and low emissions of undesirable by-products such as dioxin. These hazardous wastes generally contain chlorinated compounds. In the decomposition of chlorinated wastes, a product species desired is HCl which can be scrubbed from exhaust stream using water or alkaline solution. One of the promising methods of the destruction is utilization of thermal plasma [1, 2]. The thermal plasma has high temperature and high activity, so that the plasma will completely decompose the wastes and thermodynamically stable species such as CO<sub>2</sub> and HCl will be mainly formed.

The present study was concerned with the decomposition of chlorinated compounds using a thermal plasma fluidized bed. Chloromethane (CH<sub>3</sub>Cl) was used as a represent of chlorinated wastes since CH<sub>3</sub>Cl was the simplest chlorinated hydrocarbon. The fluidized particles were composed of calcium oxide (CaO). Since HCl reacts and is fixed in CaO bed, the exhaust gas from the decomposition will

be purified. Therefore simultaneous decomposition of  $\text{CH}_3\text{Cl}$  and recovery of  $\text{HCl}$  can take place in the reactor. This plasma fluidized bed reactor does not need a scrubber which removes  $\text{HCl}$  from products and results in the reduction of the decomposition system size as compared with the conventional plasma decomposition system [3].

## 2 Thermodynamic consideration

Thermodynamic calculation was carried out for preliminary investigation of the decomposition in the same calculation procedure as described in [4]. The results presented in Fig. 1 suggested the decomposition had to be carried out with the addition of  $\text{O}_2$  over a reactant ratio  $\text{CH}_3\text{Cl}:\text{O}_2$  of 1:1/2 because of soot production. Moreover an excess of oxygen over the ratio of 1:3/2 led to chlorine formation as shown in Fig. 2. From the calculation, the ideal reactions are written by



While the reaction of  $\text{HCl}$  with  $\text{CaO}$  is expressed as

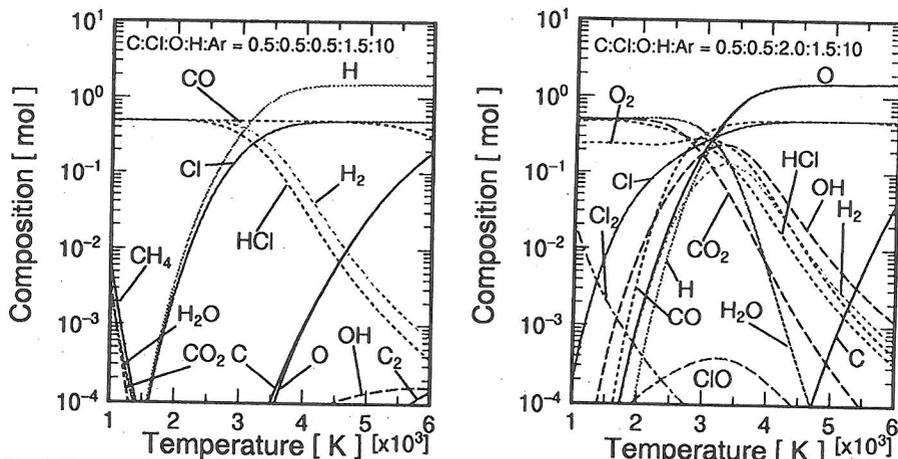
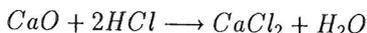


Fig.1 Equilibrium for  $\text{CH}_3\text{Cl}$  decomposition; Fig.2 Equilibrium for  $\text{CH}_3\text{Cl}$  decomposition;  
 $\text{CH}_3\text{Cl}:\text{O}_2 = 1:1/2$   $\text{CH}_3\text{Cl}:\text{O}_2 = 1:2$

## 3 Experimental

The experiment was done with the plasma fluidized bed having a conical bottom as shown in Fig. 3. Argon plasma was generated by d.c. arc discharge. The reactant

of  $\text{CH}_3\text{Cl}$  and the additive of  $\text{O}_2$  were premixed and injected into the plasma. The reacting plasma flowed through a reacting section and then into the fluidized bed. The reacting section provided sufficient reaction time before the injection into the bed and was composed of a water-cooled copper tube with an inside diameter of 8 mm and a length of 35mm. The fluidized bed was also made of a copper tube with a diameter of 30 mm and a length of 530 mm. The conical section at the bed bottom had an included angle of  $40^\circ$  and an inlet diameter of 8 mm.

Gaseous products were analyzed by gas chromatography. Qualitative analysis of chlorine element fixed in  $\text{CaO}$  bed was carried out by measuring  $\text{Cl}^-$  concentration with an ion selective electrode after dissolution of the fluidized particles in dilute nitric acid.

The experimental conditions are shown in Table 1. Commercial  $\text{CaO}$  particles with diameters of 20-100 mesh were used in the experiment. The experimental procedure was as follows: first  $\text{CaO}$  particles weighed were supplied into the fluidized bed after the discharge was started. Then the reactant and additive were introduced into the plasma. After a certain time elapsed, gaseous products were sampled and all the particles were collected for the qualitative analyses.

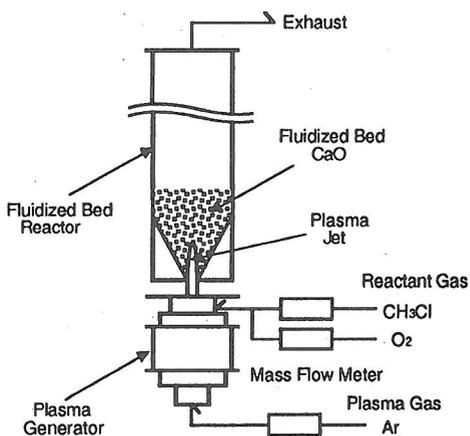


Fig. 3 Experimental apparatus

Table 1 Experimental conditons

Discharge Power		$3.2 \pm 0.2$ kW
Plasma Gas	Ar	10 l/min
Reactant Gas	$\text{CH}_3\text{Cl}$	0.3 - 1.0 l/min
	$\text{O}_2$	0.3 - 1.0 l/min
Fluidized Bed	$\text{CaO}$	50 - 100 g
	(20 - 100 mesh)	
Particle Diameter		149 - 840 $\mu\text{m}$
Discharge Time		5 - 15 min

## 4 Results and Discussion

The results showed the complete destruction of  $\text{CH}_3\text{Cl}$  took place. When  $\text{O}_2$  was added over a ratio  $\text{CH}_3\text{Cl}:\text{O}_2$  of 1:3/2, chlorine formation was confirmed by a potassium iodide starch paper test. While soot was observed below the ratio of 1:1/2. Between these ratios, the product gas consisted of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$ .

Figure 4 shows timewise variations for the recovery of Cl by CaO particles ( $R_{Cl}$ ). The recovery almost attains to 1.0 before 5 min, which means Cl is completely recovered by CaO. After 5 min, the recovery decreases with time elapsed and much initial weight of CaO improves the recovery. The curves in the figure indicate simulation results mentioned below. The conversion of CaO particles into  $\text{CaCl}_2$  ( $X_{\text{CaCl}_2}$ ) increases with time shown in Fig. 5. The lines indicate complete recovery of Cl ( $R_{Cl} = 1.0$ ). The experimental results become low as compared with the lines after 5 min, indicating incomplete recovery of Cl as shown in Fig. 4.

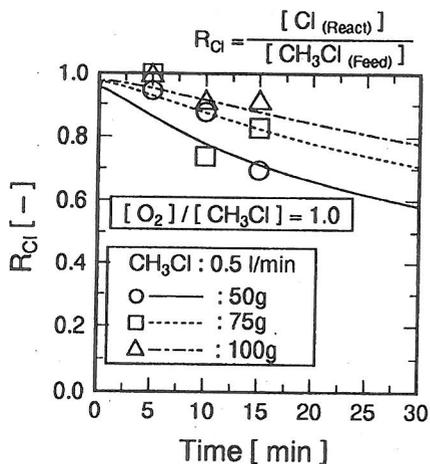


Fig.4 Timewise variations of Cl recovery

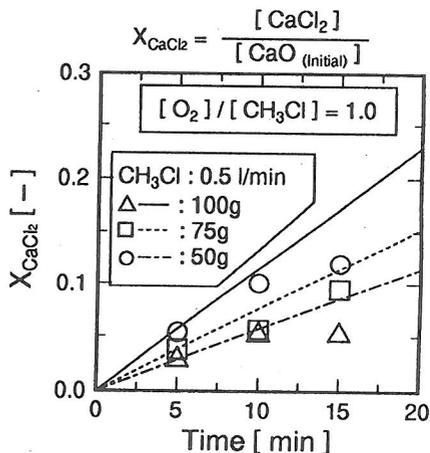


Fig.5 Timewise variations of conversion into  $\text{CaCl}_2$

Effects of  $\text{CH}_3\text{Cl}$  gas flow rate on Cl recovery are presented in Fig. 6. The reactant ratio of  $\text{O}_2$  to  $\text{CH}_3\text{Cl}$  was set to unity. The decomposition time and CaO initial weight were respectively 10 min and 100 g. The recovery decreases with gas flow rate, so that high concentration of HCl in the product gas reduces Cl recovery. Figure 7 shows effects of the reactant ratio ( $\text{O}_2/\text{CH}_3\text{Cl}$ ) on Cl recovery. The recovery is nearly constant under a ratio  $\text{CH}_3\text{Cl}:\text{O}_2$  of 1:3/2. While there is a drop in the recovery at the ratio of 2 because  $\text{Cl}_2$  is produced at this condition and the reactivity of  $\text{Cl}_2$  with CaO is lower than that of HCl.

The conversion into CO was almost independent of the decomposition time and the initial weight of CaO. Thermogravimetry for the reacted particles indicated CaO particles also reacted with  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The conversions into  $\text{CaCO}_3$ ,  $\text{CO}_2$ , and CO are shown in Figs. 8 and 9. The conversion into CO slightly increases with  $\text{CH}_3\text{Cl}$  flow rate and about half of  $\text{CO}_2$  formed is reacted with CaO (Fig. 8). While the conversion into CO decreases with increasing reactant ratio, which is consistent with the equilibrium calculation. A decrease in CO concentration in the product gas promotes conversion into  $\text{CO}_2$  and  $\text{CaCO}_3$  (Fig. 9).

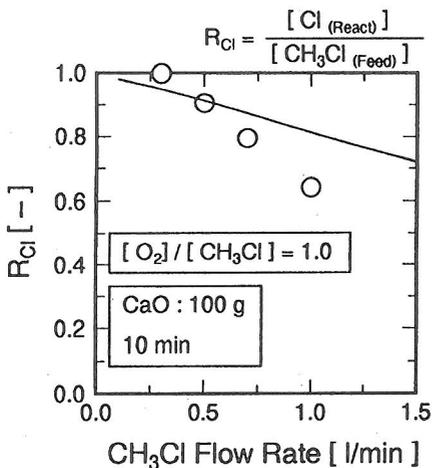


Fig.6 Effects of reactant flow rate on Cl recovery

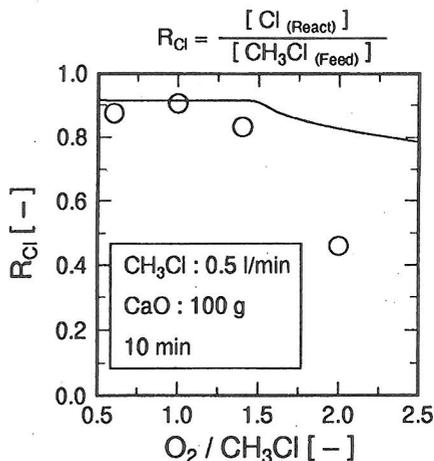


Fig.7 Effects of reactant ratio on Cl recovery

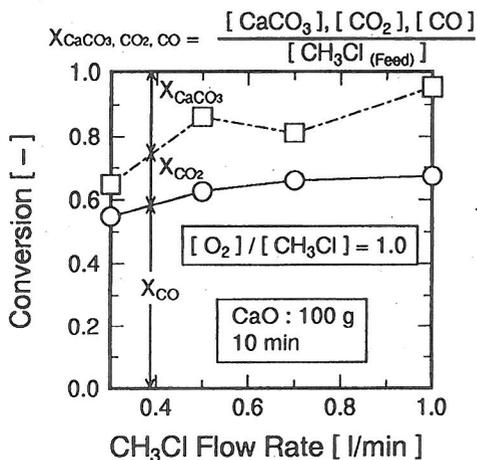


Fig.8 Effects of reactant flow rate on conversion into CO, CO<sub>2</sub>, CaCO<sub>3</sub>

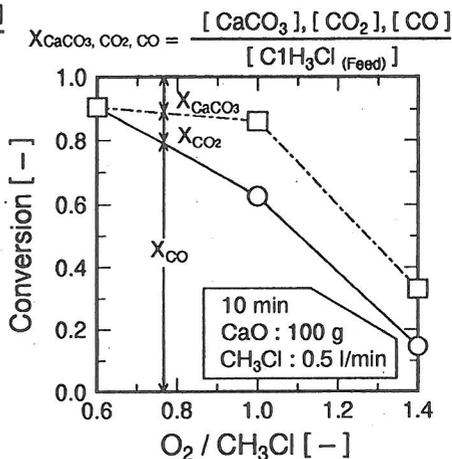


Fig.9 Effects of reactant ratio on conversion into CO, CO<sub>2</sub>, CaCO<sub>3</sub>

A simple model for the fluidized bed part was proposed including a heterogeneous reaction between CaO and HCl to explain the recovery behavior. Assumptions in the model were made as follows: (1) fluidized bed was isothermal, (2) one-dimensional distribution of HCl concentration existed in axial direction, (3) spherical CaO particles made up of spherical grains were perfectly mixed in the bed, (4) HCl only reacted with CaO and the reaction obeyed the shrinking-core model [5]. Under the assumptions, the differential equation concerning HCl con-

centration can be written as

$$\frac{\partial C_{HCl}}{\partial t} = -u \frac{\partial C_{HCl}}{\partial Z} - (1 - \epsilon_f) k_r C_{HCl} \quad (1)$$

where  $C_{HCl}$ ,  $u$ , and  $\epsilon_f$  respectively denote HCl concentration, gas velocity, and void fraction. While  $k_r$  is reaction rate and expressed by

$$k_r = \frac{3}{2r_g^3(1/D_s(1/r_c - 1/r_g) + 1/(k_s r_c^2))} \quad (2)$$

where  $r_g$ ,  $r_c$ ,  $D_s$ , and  $k_s$  respectively mean radius of grain, radius of unreacted core, diffusion coefficient, and intrinsic rate constant for first-order reaction of HCl. The calculation was carried out by discretization of Eq.(1). The initial condition was determined from the equilibrium concentration.

The calculated results indicated by the curves in Figs. 4, 6, and 7 show qualitative agreement with the experimental ones. The decreases in the recovery with time and  $CH_3Cl$  flow rate were ascribed to reactant diffusion control through a developing product layer in CaO particles. While chlorine formation in the equilibrium over the reactant ratio of 1.5 reduced the recovery because chlorine was assumed not to react with CaO. The model described here will be developed for further study about destruction and recovery mechanisms in the plasma fluidized bed.

Considering the results described above, simultaneous decomposition of  $CH_3Cl$  and recovery of Cl are possible in the reactor presented here. Moreover the reactor can fix  $CO_2$  which also affects global environment. Generally thermal plasma can easily decompose halocarbons into thermodynamically stable species, the plasma fluidized bed reactor, therefore, can be adapted to the destruction of halogenated waste without undesirable products emission.

## 5 Conclusion

The decomposition of  $CH_3Cl$  was carried out using the plasma fluidized bed where CaO was used as fluidized particles. The experimental results indicated the simultaneous decomposition of  $CH_3Cl$  and recovery of Cl took place. The recovery mechanisms were explained with a simple model including the heterogeneous reaction between CaO and HCl. The study concluded the plasma fluidized bed was effective for the destruction of chlorinated compounds.

## References

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