DECOMPOSITION OF DIOXINS IN FLY ASH WITH SUPERCRITICAL WATER OXIDATION

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Keywords: Supercritical Water Oxidation, Decomposition, Dioxin, Fly Ash

Introduction

Dioxin is the general term for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) shown in **Fig. 1**. They are highly toxic compounds even in trace amounts, and detected in combustion sources such as municipal waste incinerators and in bleaching processes of pulp mills. A recent EPA study has concluded that up to 50% of the known dioxin sources in the environment may be derived from municipal waste incinerators (Hileman *et al.*, 1994).

Several techniques have been proposed for the decomposition of chemically stable dioxins: (1) combustion with melting treatment of fly ash, (2) dechlorinating thermal decomposition in atmosphere with a low concentration of oxygen, (3) photo decomposition with sun light or ultraviolet irradiation, and (4) decomposition with microorganisms. The main requirement for disposal techniques is that they are, safe simple and rapid. Each technique has some drawbacks in industrial use. For melting treatment (Hirth *et al.*, 1989), much energy is required to maintain a high temperature of more than 1500 K and volatile heavy metals such as mercury have to be recovered with a condensation process. For the second method (Hagenmaier *et al.*, 1987), the reverse reaction of the reproduction of the dioxins occurs when the oxygen concentration increases. For the third (Esposito *et al.*, 1980) and fourth (Matsumura *et al.*, 1983) methods, the reaction is very slow and it is difficult to decompose the dioxins completely.

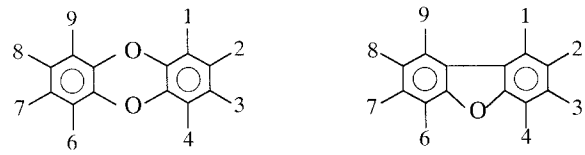


Fig. 1 Molecular structures of dioxins

Waste treatment using supercritical water, which exists as a phase above the critical temperature (647.3 K) and critical pressure (22.12 MPa), has been

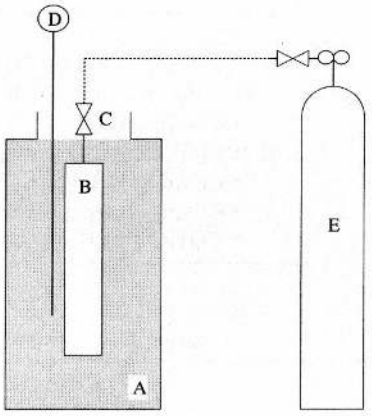
* Received on October 2, 1996. Correspondence concerning this article should be addressed to T. Sako.

investigated for ten years. This technique has advantages to decompose hazardous wastes: (1) both water and the oxidizer are clean and safe materials, and (2) powerful decomposition properties are realized for toxic organics. The method has been applied to the decomposition of dioxins in a pulp mill sludge and more than 99% of the dioxins were decomposed under the conditions that the temperature was above 773 K, the pressure was around 25 MPa and the reaction time was less than 10 min (Modell *et al.*, 1992; Swallow and Killilea, 1992; Blaney *et al.*, 1995).

In this study, we tried to decompose the dioxins in a fly ash using supercritical water and an oxidizer. The first objective is to compare the decomposition efficiency of the dioxins in the fly ash with that in the pulp mill sludge, because the distribution pattern of the dioxin isomers in the fly ash (called "incineration pattern") is quite different from that in the pulp mill sludge ("pulp bleaching pattern") (Hiraoka, 1993a), that is, the former has many kinds of dioxin isomers and the latter contains relatively high concentrations of tetrachlorodibenzofuran and tetrachlorodibenzo-p-dioxin. The second objective is to check the possibility of the decomposition of dioxins at around 673 K because a conventional stainless steel can be used as a construction material for the decomposition reactor in a very dilute aqueous region of hydrogen chloride. The third objective is to examine what kind of oxidizer is suitable for rapid and complete decomposition of the dioxins.

1. Experimental

A batch-type reactor made of 316 stainless steel, and with an inner volume of 20 cm^3, was used for decomposition of the dioxins found in fly ash discharged from a municipal waste incinerator. The experimental apparatus is shown in **Fig. 2**. The reactor (B) was immersed into a molten salt bath (A) filled with sodium nitrite. The whole reactor was kept in the molten salt except for the stop valve (C) to avoid the partial condensation of water. The reaction temperature was considered to be equal to the temperature of the molten salt bath, which was measured with a K-type thermocouple (D) inserted into the molten salt bath. The reaction pressure was calculated from the pvT relation of pure water (Japan Society of Mechanical Engineers, 1994), where the supercritical water was considered to be a pure component because only trace amounts of organic compounds were dissolved in the supercritical water, and the molar volume of water v was determined from the charged amount of water and the inner volume of the reactor. The reaction time "zero" was defined to be the time when the temperature of the reactor reached a given reaction temperature. It took about



A: Molten salt bath D: Thermometer
B: Reactor E: Oxygen gas cylinder
C: Stop valve

Fig. 2 Apparatus for decomposition of dioxins

5 min to increase the temperature of the reactor from the room temperature to 673 K.

2 g of fly ash and about 7.4 g of water, which was adjusted so that the reaction pressure would be 30 MPa, were charged into the reactor and an oxidizer such as an air, oxygen gas or hydrogen peroxide was added into the reactor. Then the reactor was immersed into the molten salt bath maintained at reaction temperature. After keeping the reactor at the reaction temperature for a given time interval, the reactor was taken out of the molten salt bath and cooled in water quickly to stop the reaction as soon as possible. The reactor was subsequently opened and the fly ash and water were taken from the reactor.

The dioxins were analyzed by Sumika Chemical Analysis Service Co., Ltd. according to the method of Japan Waste Research Foundation (Hiraoka, 1993b). The sample was a slurry of the fly ash and water. At first, the slurry was separated into the liquid and solid components. Prior to the analysis, both samples were treated with hydrochloric acid, extracted with toluene, mixed together, treated with sulfuric acid, cleaned up with a column chromatograph, and concentrated. Then the dioxins in the sample were analyzed using a GC/MS with a high sensitivity. The column arrangements are presented in **Table 1**. The analytical error of the dioxins was within $\pm 5\%$ and, as a result, the maximum error of the total decomposition yield in **Table 2** was 0.2%.

The oxygen gas was provided by Iwatani Industries Co, Ltd. and its purity was more than 99.9%. The hydrogen peroxide aqueous solution was supplied by Santoku Chemical Industries, Ltd. and the impurities, except for water, were less than 0.1%. Water, which was deionized, distilled and deaired with nitrogen gas, was used in all experiments.

Table 1 Column arrangements of GC/MS systems

1. $PCDD_S$ and $PCDF_S$ substituted by 4 – 6 chlorine atoms
   - Column: SP-2331 fused silica column (60 m×0.25 mmID)
   - Column temp.: 373 K (1 min.) – 473 K (30 K/min.) – 523 K (3 K/min. and hold)
   - Carrier gas: He
2. $PCDD_S$ and $PCDF_S$ substituted by 7 – 8 chlorine atoms
   - Column: DB-5 cross-linked phenyl methyl silicone
   - Column temp.: 373 K (1 min.) – 493 K (30 K/min.) – 573 K (5 K/min. and hold)
   - Carrier gas: He

Table 2 Decomposition of dioxins with supercritical water+oxidizer

		Charged fly ash	R-1	R-2	R-3	R-4
T	[K]	—	673	673	673	673
p	[MPa]	—	30	30	30	30
Time	[min.]	—	15	30	30	30
Charged fly ash	[g]	—	2.00	2.00	2.00	2.00
Charged water	[g]	—	7.57	7.33	7.54	7.30
Oxidizer	[ng/g]	—	0.1 MPa Air	0.1 MPa Air	0.5 MPa O_2	0.02%H_2O_2
T_4CDD	[ng/g]	2.0	1.1	1.2	0.27	0.035
P_5CDD	[ng/g]	5.9	0.26	0.25	0.79	0
H_6CDD	[ng/g]	12.1	0.07	0.12	0.10	0.18
H_7CDD	[ng/g]	34	0.075	0.035	0.15	0
O_8CDD	[ng/g]	38	0.05	0.085	0.04	0.025
Total PCDD	[ng/g]	92	1.55	1.69	1.41	0.24
Decomp. yield	[%]	—	98.3	98.2	98.5	99.7
T_4CDF	[ng/g]	5.5	3.15	2.64	0.79	0.20
P_5CDF	[ng/g]	8.7	1.00	0.29	0.30	0.02
H_6CDF	[ng/g]	2.8	0.24	0.20	0.28	0.095
H_7CDF	[ng/g]	38	0.025	0	0.05	0
O_8CDF	[ng/g]	37	0.02	0.015	0	0.005
Total PCDF	[ng/g]	92	4.43	3.14	1.42	0.32
Decomp. yield	[%]	—	95.2	96.6	98.5	99.7
Sum of PCDD+PCDF	[ng/g]	184	5.98	4.83	2.83	0.56
Total decomp. yield	[%]	—	96.8	97.4	98.5	99.7

$$\text{Total decomp. yield [\%]} = \left(1 - \frac{\text{Residue of PCDD + PCDF}}{\text{Charged PCDD + PCDF}}\right) \times 100$$

T_4CDD = tetrachlorodibenzo-*p*-dioxin
P_5CDD = pentachlorodibenzo-*p*-dioxin
H_6CDD = hexachlorodibenzo-*p*-dioxin
H_7CDD = heptachlorodibenzo-*p*-dioxin
O_8CDD = octachlorodibenzo-*p*-dioxin

T_4CDF = tetrachlorodibenzofuran
P_5CDF = pentachlorodibenzofuran
H_6CDF = hexachlorodibenzofuran
H_7CDF = heptachlorodibenzofuran
O_8CDF = octachlorodibenzofuran

2. Results and Discussion

The dioxins were decomposed with supercritical water and an oxidizer such as air, pure oxygen gas or hydrogen peroxide. The total concentration of the dioxins in the fly ash was 184 ppb. The concentration of each compound is presented in the first column of Table 2. The stoichiometric mass of the oxygen was calculated to be 0.28 μg from the analytical results of the dioxins to be decomposed. The experimental results for the decomposition are also presented in Table 2. Air was used as the oxidizer in R-1 and 2; pure oxygen gas in R-3; and hydrogen peroxide in R-4.

In R-1 and 2, the charged air corresponded with about 10,000 times the stoichiometric oxygen necessary to decompose the dioxins in the fly ash completely. We could decompose around 97% of the dioxins. The decomposition yield of PCDD is a little higher than that of PCDF and the chlorinated

compounds with more chlorine atoms are decomposed more easily with the supercritical water oxidation technique. When the reaction time was increased from 15 to 30 min, the decomposition yield increased a little.

Oxidizers stronger than the air are required to achieve complete decomposition of the dioxins. Pure oxygen gas (0.5 MPa) is used in R-3 to promote the oxidative decomposition of the dioxins. An improvement of total decomposition yield from 97.4% to 98.5% is obtained. The reason for higher decomposition yield is that the T_4CDD and T_4CDF are decomposed more and the decomposition yield of the PCDF increases from 96.6 to 98.5%.

Next the hydrogen peroxide, which is the strongest oxidizer in this work, was added into the supercritical water in R-4. This oxidizer has no adverse environmental effects because it decomposes to water and oxygen. It also produces a nascent oxygen which is very reactive and oxidizes organic compounds rapidly. In R-4, we added about 2,500 times the oxygen theoretically required stoichiometrically. Judging from the experimental results, supercritical water with hydrogen peroxide is a powerful solvent to decompose the dioxins.

Conclusion

The dioxins in the fly ash were decomposed almost completely using the supercritical water oxidation technique under the conditions in which the reaction temperature, pressure and time were 673 K, 30 MPa and 30 min, respectively. The reaction temperature was lower, the reaction pressure was a little higher and the reaction time was longer, comparing with the previous work on the treatment of dioxins in pulp mill sludge. The reaction temperature in this study is low enough to use a conventional stainless steel as the construction material of the reactor. The effect of the oxidizers becomes stronger in the order, air, pure oxygen gas, and hydrogen peroxide. The maximum decomposition yield of the dioxins is 99.7% when using supercritical water +0.02 wt% hydrogen peroxide.

Nomenclature

p	=	pressure	[MPa]
PCDD	=	polychlorinated dibenzo-*p*-dioxin	
PCDF	=	polychlorinated dibenzofuran	
T	=	temperature	[K]
v	=	molar volume	[m^3/mol]

Literature Cited

Blaney, C.A., L. Li, E.F. Gloyna and S.U. Hossain; "ACS Symp. Ser. 608 Innovations in Supercritical Fluids," p. 444-455, ACS, Washington, DC, USA (1995)

Esposito, M.P., T.O. Tiernan and F.E. Dryden; "Dioxins," EPA Report, No. 600/2-80-197, p. 233-241 (1980)

Hagenmaier, H., M. Kraft and H. Brunner and R. Haag; "Catalytic Effects of Fly Ash from Waste Incineration Facilities on the Formation and Decomposition of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans," *Environ. Sci. Technol.*, **21**, 1080-1084 (1987)

Hileman, B., J.R. Long and E.M. Kirschner; "Chlorine Industry Running Flat Out Despite Persistent Health Fears," *Chem. Eng. News*, **72** (Nov. 21), 12 (1994)

Hiraoka, M. (Ed.); "Waste Treatment and Measures Against Dioxins," p. 8-9, Kankyo Kogai Shinbunsha, Tokyo, Japan (1993a)

Hiraoka, M. (Ed.); "Waste Treatment and Measures Against Dioxins," p. 359-379, Kankyo Kogai Shinbunsha, Tokyo, Japan (1993b)

Hirth, M., CH. Wieckert, J. Jochum and H. Jodeit; Preprints of Recycling International, vol. 2, p. 1561-1566, EF-VERLAG fur Energie-und Umwelttechnik GmbH, Berlin, Germany (1989)

Matsumura, F., J. Quensen and G. Tsushimoto; "Microbial Degradation of TCDD in a Model Ecosystem," *Environ. Sci. Res.*, **26**, 191-219 (1983)

Modell, M., J. Larson and S.F. Sobczynski; "Supercritical Water Oxidation of Pulp Mill Sludges," *Tappi J.*, **75**, 195-202 (1992)

Swallow, K.C. and W.R. Killilea; "Comment on Phenol Oxidation in Supercritical Water: Formation of Dibenzofuran, Dibenzo-*p*-dioxin, and Related Compounds," *Environ. Sci. Technol.*, **26**, 1849-1850 (1992)

The Japan Society of Mechanical Engineers; "JSME Steam Tables," JSME, Tokyo, Japan (1994)