Decomposition Process for Polychlorobiphenyls by Means of Basic Molten Salts

Yasufumi YOKKA,1,2) Masayoshi KIMURA,1,3) Takeshi HANDA,1,4) Kohei SASAKI,1,5) Osamu TAKEDA,1)* Tsutomu YAMAMURA1) and Yuzuru SATO1)

1) Tohoku University, 6-6-02 Aramaki-Aza-Aoba, Aoba-ku, Sendai, 980-8579 Japan. 2) Formerly Graduate Student, Tohoku University. Now at IHI Co., 3-1-1, Toyosu, Koto-ku, Tokyo, 135-8710 Japan. 3) Formerly Under Graduate Student, Tohoku University. Now at Furukawa Electric Co. Ltd., 2-2-20, Higashi-shinagawa, Shinagawa-ku, Tokyo, 140-8628 Japan. 4) Formerly Under Graduate Student, Tohoku University. Now at Nippon Light Metal Company, Ltd., 2-2-20, Higashi-shinagawa, Shinagawa-ku, Tokyo, 140-8628 Japan. 5) Formerly Under Graduate Student, Tohoku University. Now at Mitsubishi Materials Co., 1-3-2, Ote-machi, Chiyoda-ku, Tokyo, 100-8117 Japan.

(Received on March 7, 2012; accepted on May 21, 2012)

The decomposition of polychlorobiphenyls (PCBs) by means of basic molten salts was investigated in order to construct a safe, simple and highly efficient waste treatment system for PCBs. PCBs (mono, di, tri, tetra, penta, hexa, hepta-chlorobiphenyls) solution was injected into basic molten salts (KOH–K2CO3 or NaOH–Na2CO3) at 773–973 K with oxygen or imitation air. The mass of residual PCBs in the exhaust after the decomposition and the mass of PCBs condensed inside the reaction vessel were measured by using gas chromatograph mass spectrometry, and the decomposition efficiency of PCBs was determined. The decomposition efficiency was also determined from the residual concentration of PCBs in the exhaust in some experiments. The decomposition efficiency was high regardless of the number of chlorine contained in PCBs and reached to very high of 99.999% in an optimum condition. Chlorine of PCBs was captured in basic molten salts, and organic compounds containing chlorine was not emitted from the molten salts. Some by-products comprising benzene rings were found at 773–873 K, but the by-products disappeared at 973 K.

KEY WORDS: PCB; waste treatment; decomposition; basic molten salts.

1. Introduction

The waste treatment of polychlorobiphenyls (PCBs) with strong toxicity has been desired for long time, but the complete treatment has not yet been realized because PCBs have very tough chemical structure and there is a risk of the formation of dioxins during the treatment.1) The waste treatment is in progress at the initiative of Japanese government, but a large amount of PCBs is still left.2) The authors have ever carried out fundamental studies for developing a safe, simple and highly efficient waste treatment process for PCBs by means of basic molten salts.3,4) The schematic illustration of the decomposition reaction is shown in Fig. 1. In this process, PCBs are introduced into basic molten salts where the chlorine of PCBs as an acidic element is absorbed in the molten salt and the organic components of PCBs are oxidized by oxygen. This waste treatment technology by using molten salts was originated from the study for the waste treatment of chemical weapons in USA since 1960s.5) The process was then developed for many persistent organic wastes in USA,6,7) Japan,8,9) and Korea.10–14)

The advantages of utilization of molten salts are summarized as follows: (1) no dioxins are formed due to gas/liquid separation, and only simple harmless products (CO2 and H2O) are emitted; (2) operation temperature is considerably lower than that in the conventional incineration, and the temperature control is easy because of the reaction in condensed phase; (3) decomposition treatment is carried out under atmospheric pressure; (4) handling of chlorine absorber (molten salts) is easy.

The authors have studied the decomposition of carbontet-

Fig. 1. The schematic illustration of decomposition reaction of polychlorinated biphenyls (PCBs, C12H10–xClx, x = 1–10) by using basic molten salts.
rachloride (CCl₄)³ and mono-, di- and tri-chlorobenzens⁴ as a simple chlorinated organic compound prior to the decomposition of PCBs. As the results, CCl₄ was destructed at high decomposition efficiency over 99.9% at relatively low temperature (673–973 K) without oxygen. Furthermore, the chlorobenzens were destructed at very high decomposition efficiency of 99.9999% in an optimum condition with oxygen. Based on the previous studies, some PCB congeners (mono, di, tri, tetra, penta, hexa, hepta-chlorobiphenyls) were selected in this study, and their decomposition was investigated by using basic molten salts.

2. Experimental

2.1. Chemicals

The PCBs containing 1 to 7 chlorine (>99%, AccuStandard Inc.) were individually used for the decomposition experiment as the sample. The name, structural formula and physical properties of the chemicals used in this study are summarized in Table 1.15–21 As shown in the table, all the PCBs used are solid at room temperature, and they are difficult to feed as it is. The PCBs were then dissolved in an organic solvent, n-nonane (>98%, Wako Pure Chemical Industries Ltd.) to be subjected to the experiment as a solution. The concentration of PCBs in the sample solution was 2–20 mg·(ml-nonane)⁻¹. In the control experiment without molten salts, the concentration of PCBs in the sample solution was 0.04–0.06 mg·(ml-nonane)⁻¹.

Since molten salts used for the decomposition of PCBs should be basic to absorb chlorine and has oxidizing ability to decompose organic components, the mixture of KOH (>85%, Wako Pure Chemical Industries Ltd.) and K₂CO₃ (>99.5%, Wako Pure Chemical Industries Ltd.) was used. The eutectic mixture of NaOH (>97%, Wako Pure Chemical Industries Ltd.) and Na₂CO₃ (>99.8%, Wako Pure Chemical Industries Ltd.) was also used for comparison. The composition of the salts was eutectic (KOH–9.3 mol% K₂CO₃, NaOH–8.3 mol% Na₂CO₃). Most of absorbed water in the mixed salt was preliminarily removed by introducing argon into the melt until the fume from the melt disappeared because water in the salt hinders the decomposition of PCBs. Additionally, hydroxide also decomposes to evolve a trace of water. For instance, KOH decomposes with following reaction.

$$KOH (l) = 1/2 K_2O (l) + 1/2 H_2O (g)$$............ (1)

The equilibrium constant K is calculated from the thermodynamic data as follows.²¹

$$K = a_{KOH}^{1/2} a_{H_2O}^{1/2} / a_{K_2O} = 2.58 \times 10^{-5}$$ at 773 K...... (2)

When $a_{KOH}$ is almost 1 and $a_{K_2O}$ is 0.001, $p_{H_2O}$ is 6.64×10⁻⁷ atm. This means that the water formed by the decomposition of hydroxide is negligible. Therefore, the salt had nearly no water at the start of the experiment.

2.2. Experimental Apparatus and Analysis

Experimental apparatus and the procedure were reported in the previous paper.⁴ PCB solution was supplied by a syringe pump at the rate of 5 μl·min⁻¹, and imitation air (N₂–21% O₂) or oxygen was supplied by a mass flow controller at the rate of 20–60 ml·min⁻¹. The coaxial stainless steel tubes for the introduction of PCBs were identical to the previous ones.

$$Ka p a = × − Ka p a$$

Table 1. Chemicals used in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Structural formula</th>
<th>Molecular weight, M/г·mol⁻¹</th>
<th>Melting point, Tm/K</th>
<th>Boiling point, Tb/K</th>
<th>Vapor pressure of solid, p/mPa at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-monochlorobiphenyl</td>
<td>C₁₂H₉Cl</td>
<td>Cl – Cl – Cl – Cl</td>
<td>188.6</td>
<td>349ᵃ</td>
<td>566ᶜ</td>
<td>UNK</td>
</tr>
<tr>
<td>4,4’-dichlorobiphenyl</td>
<td>C₁₂H₈Cl₂</td>
<td>Cl – Cl – Cl – Cl</td>
<td>223.1</td>
<td>422ᵇ</td>
<td>590ᶜ</td>
<td>3.2ᵇ</td>
</tr>
<tr>
<td>2,4’,5-trichlorobiphenyl</td>
<td>C₁₂H₇Cl₃</td>
<td>Cl – Cl – Cl – Cl</td>
<td>257.5</td>
<td>340ᵃ</td>
<td>UNK</td>
<td>11.7ᵇ</td>
</tr>
<tr>
<td>2,2’,4,4’-tetrachlorobiphenyl</td>
<td>C₁₂H₆Cl₄</td>
<td>Cl – Cl – Cl – Cl</td>
<td>292.0</td>
<td>314ᵃ</td>
<td>UNK</td>
<td>UNK</td>
</tr>
<tr>
<td>2,2’,4,5,5’-pentachlorobiphenyl</td>
<td>C₁₂H₅Cl₅</td>
<td>Cl – Cl – Cl – Cl</td>
<td>326.4</td>
<td>350ᵃ</td>
<td>UNK</td>
<td>UNK</td>
</tr>
<tr>
<td>2,2’,4,4’,6,6’-hexachlorobiphenyl</td>
<td>C₁₂H₄Cl₆</td>
<td>Cl – Cl – Cl – Cl</td>
<td>360.9</td>
<td>387ᵇ</td>
<td>UNK</td>
<td>UNK</td>
</tr>
<tr>
<td>2,2’,3,4,4’,5,5’-heptachlorobiphenyl</td>
<td>C₁₂H₃Cl₇</td>
<td>Cl – Cl – Cl – Cl</td>
<td>395.3</td>
<td>383ᵇ</td>
<td>UNK</td>
<td>0.013ᵇ</td>
</tr>
<tr>
<td>n-nonane</td>
<td>C₉H₂₀</td>
<td></td>
<td>128.3</td>
<td>220ᵇ</td>
<td>424ᵈ</td>
<td>593×10⁻³ᶜ</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>KOH</td>
<td>–</td>
<td>56.1</td>
<td>677ᵃ</td>
<td>1594ᶠ</td>
<td>–</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>K₂CO₃</td>
<td>–</td>
<td>138.2</td>
<td>1174ᵈ</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>–</td>
<td>40.0</td>
<td>593ᵇ</td>
<td>1828ᶠ</td>
<td>–</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>–</td>
<td>106.0</td>
<td>1131ᵇ</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>


1915 © 2012 ISIJ
ious ones. The gas nozzle made of alumina was also same and was immersed into the molten salts in the depth of 50 mm from the surface level.

The PCBs introduced into the molten salts was estimated to form a bubble to be reacted with the molten salts during the lifting as Eqs. (3) and (4) under excess oxygen condition (trichlorobiphenyl is used as an example).

\[
\text{C}_12\text{H}_8\text{Cl}_3 (g) + 3 \text{ KOH} (l) + 13 \text{ O}_2 (g) \\
\rightarrow 3 \text{ KCl} (l) + 5 \text{ H}_2\text{O} (g) + 12 \text{ CO}_2 (g) \text{......... (3)} \\
\Delta G^\circ_{(3)} = -6347 \text{ kJ at 673 K}^{20,21} \\
\Delta G^\circ_{(3)} = -6374 \text{ kJ at 973 K}^{20,21}
\]

\[
\text{C}_12\text{H}_7\text{Cl}_3 (g) + 3/2 \text{ K}_2\text{CO}_3 (l) + 13 \text{ O}_2 (g) \\
\rightarrow 3 \text{ KCl} (l) + 7/2 \text{ H}_2\text{O} (g) + 27/2 \text{ CO}_2 (g) \text{......... (4)} \\
\Delta G^\circ_{(4)} = -6117 \text{ kJ at 673 K}^{20,21} \\
\Delta G^\circ_{(4)} = -6231 \text{ kJ at 973 K}^{20,21}
\]

It was expected that the chlorine in the PCBs is trapped as KCl and the exhaust contains only H\text{2}O and CO\text{2}. Similar reactions were expected in the sodium salt mixture. It was also expected that the n-nonane as the solvent was converted to H\text{2}O and CO\text{2} by reacting with oxygen. The ratio of the oxygen supply to the solution was more than 1.5 times of stoichiometry for the complete decomposition.

The exhaust after the decomposition was sampled, and the residual concentration of PCBs and the chemical species of by-products were analyzed by a gas chromatography mass spectrometer (GC-MS, Shimazu Co., GCMS-QP2010). Total residual mass of PCBs in the exhaust, w\text{E} was calculated from the concentration and the total volume of introduced gas.

In this study, sampling method was changed from not only exhaust but also condensed matter by considering low vapor pressure of PCBs. Therefore, the inside of the alumina crucible, the outside of the alumina nozzle and the inside of the stainless steel cap were rinsed with n-hexane after the experiment, and the concentration of PCBs in the hexane solution was also analyzed by the GC-MS. Total mass of PCBs condensed inside the reaction vessel, w\text{R} was calculated from the concentration determined. The decomposition efficiency of PCBs by the basic molten salts, \( \varepsilon \) was evaluated by the following equation in this study.

\[
\varepsilon = \left[ 1 - \left( \frac{w\text{E} + w\text{R}}{w_1} \right) \right] \times 100 ...................(5)
\]

where \( w_1 \) indicates the mass of the PCBs fed.

In the experiments for \( \text{C}_12\text{H}_3\text{Cl}_2 \), the decomposition efficiency, \( \varepsilon' \) was evaluated from the residual concentration of PCBs in the exhaust (C\text{I}) and the concentration of PCBs in the gas mixture fed initially (C\text{I}) as shown in Eq. (6).

\[
\varepsilon' = \left( 1 - \frac{C\text{I}}{C\text{I}} \right) \times 100 ....................... (6)
\]

The concentration indicates the volume fraction (vol-ppm) of chemicals in the carrier gas at 25°C under 1 atm calculated from the mass of PCBs.

3. Results and Discussion

3.1. Oxidation without Molten Salts

The influence of oxidation of PCBs without molten salts was preliminary checked. The residual concentration of dichlorobiphenyl (\( \text{C}_{12}\text{H}_{4}\text{Cl}_2 \)) in the exhaust after the injection with oxygen into the empty crucible at 673–873 K is shown in Fig. 2. The concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in the exhaust contains only H\text{2}O and CO\text{2}. Similar reactions were expected in the sodium salt mixture. It was expected that the chlorine in the PCBs is trapped as KCl and the exhaust contains only H\text{2}O and CO\text{2}. The concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in the exhaust after the injection with air into the empty crucible at 773–973 K is shown in Fig. 3. The concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in the nonane solution was relatively low of 0.06 mg·ml\text{–}1, and the total mass of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) fed was 27 mg. As shown in the figure, the mass in the exhaust decreased with increasing temperature and reached to about 0.2 mg. This corresponds to the decomposition efficiency of 99%. The higher efficiency may be due to higher temperature.

![Fig. 2](image)

**Fig. 2.** The residual concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in the exhaust after the thermal decomposition without molten salts. Carrier gas: oxygen, concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in solution: 0.04 mg·(ml-nonane)\text{–}1, injection rate of solution: 5 \( \mu \text{L} \cdot \text{min}^{-1} \), flow rate of oxygen: 20 ml·min\text{–}1, initial concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 : 1.1 \text{ vol-ppm.} \)

![Fig. 3](image)

**Fig. 3.** The residual mass of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in the exhaust after the thermal decomposition without molten salts. Carrier gas: imitation air, concentration of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) in solution: 0.06 mg·(ml-nonane)\text{–}1, injection rate of solution: 5 \( \mu \text{L} \cdot \text{min}^{-1} \), flow rate of imitation air: 20 ml·min\text{–}1, total mass of \( \text{C}_{12}\text{H}_7\text{Cl}_3 \) fed: 27 mg.
Duvall and Rubey carried out the decomposition experiment for PCB congeners with air for the exposure time of about 1 second. They reported that the decomposition efficiencies of 2,2',5,5'-tetrachlorobiphenyl (C_{12}H_{6}Cl_{4}) and 2,2',4',5,5'-pentachlorobiphenyl (C_{12}H_{5}Cl_{5}) at 995 K were 99.3% and 99.9%, respectively. The decomposition efficiency obtained in this study was similar to that obtained by Duvall and Rubey. This indicates that the decomposition by the air at moderate temperature was not enough for complete decomposition.

As described above, oxidation without molten salts was not enough for complete decomposition. If the reaction temperature is increased, the decomposition efficiency should increase. However, a risk of the formation of dioxins in the exhaust during the cooling step is left. Figure 4 shows a GC-MS spectrum of the exhaust after the thermal decomposition of C_{12}H_{7}Cl_{3}. Representative by-products are also shown in the figure. As shown in the figure, aromatic compounds such as benzene and toluene were formed. These compounds might be formed by the destruction of biphenyl skeleton. Furthermore, the chlorinated compound, 1-chloroindane (compound D), was observed. This means that there is a possibility of formation of harmful chlorinated compounds by recombination reaction and that the chlorine should be separated from the exhaust containing organic compounds.

### 3.2. Decomposition of PCBs by Basic Molten Salts

The residual concentration of C_{12}H_{8}Cl_{2} in the exhaust after the decomposition by molten salt (KOH–9.3 mol% K_{2}CO_{3}) with oxygen is shown in Fig. 5. The decomposition efficiency is also shown on right ordinate in the figure. The concentration of C_{12}H_{8}Cl_{2} in the nonane solution was 2.0 mg·ml^{-1} and higher than that in the thermal decomposition experiment. The initial concentration of C_{12}H_{8}Cl_{2} in the gas was 55 vol-ppm. As shown in the figure, the concentration of C_{12}H_{8}Cl_{2} decreased less than 2.5 vol-ppb, and the decomposition efficiency more than 99.995% was established. The decomposition efficiency reached 99.999% in an optimum condition.

Furthermore, the qualitative analysis of by-products in the exhaust was carried out. Figure 6 shows the GC-MS spectrum of the exhaust after the decomposition of only n-nonane (solvent) by molten salts with air. The representative by-products are also shown in the figure. As shown in the figure, some saturated cyclic organic compounds containing oxygen were observed. Aromatic compounds were not observed. The number of species of by-products was less. Figure 7 shows the GC-MS spectrum for the decomposition of C_{12}H_{8}Cl_{2} solution by molten salts with air. In this case, some aromatic compounds such as benzene and toluene were observed. These unsaturated compounds might be formed during the decomposition step of C_{12}H_{8}Cl_{2} or during the recombination reaction of the degraded products. The by-products decreased with increasing temperature, and most of by-products disappeared at 973 K. The result of quantitative analysis for the representative by-products (benzene, toluene, styrene, naphthalene) is shown in Fig. 8. The concentration of the by-products increased with increasing temperature from 773 K to 873 K and decreased with increasing temperature to 973 K. It was expected that the concentration of the by-products monotonically decreased with increasing temperature before the experiment. But up-and-down change in the concentration was...
actually observed. This may be because the dechlorination of PCBs sufficiently progressed but the destruction of biphenyl skeleton and the formation of by-products such as benzene were not enough at 773 K. By increasing temperature, the destruction of biphenyl skeleton and the formation of by-products might sufficiently progress at 873 K. Furthermore, most of the by-products might also be destructed at 973 K.

The residual mass of C_{12}H_{7}Cl_{3} in the exhaust and inside the reaction vessel after the decomposition by using molten salts with air. Salt: KOH–9.3 mol% K\textsubscript{2}CO\textsubscript{3}. Representative by-products determined by qualitative analysis are also shown.

The residual concentration of some by-products in the exhaust after the decomposition of C_{12}H_{8}Cl_{2} solution by using molten salts. Salt: KOH–9.3 mol% K\textsubscript{2}CO\textsubscript{3}. Representative by-products determined by qualitative analysis are also shown.

The residual mass of C_{12}H_{7}Cl_{3} in the exhaust and in the reactor after the decomposition by using molten salts (average of 2 experiments). Salt: KOH–9.3 mol% K\textsubscript{2}CO\textsubscript{3}. Carrier gas: imitation air, concentration of C_{12}H_{7}Cl_{3} in solution: 10 mg (ml-nonane), injection rate of solution: 5 \mu l·min\textsuperscript{-1}, flow rate of imitation air: 60 ml·min\textsuperscript{-1}, total mass of C_{12}H_{7}Cl_{3} fed: 4 500 \mu g.

The decomposition efficiency of C_{12}H_{7}Cl_{3} by means of different compositions of molten salts (KOH–9.3 mol% K\textsubscript{2}CO\textsubscript{3} and NaOH–8.3 mol% Na\textsubscript{2}CO\textsubscript{3}) at 773–973 K is shown in Fig. 10. The decomposition efficiency was higher than 99.995% at any temperature in the potassium salt system and reached to 99.999% at 873 K on average. In the sodium salt system, the decomposition efficiency was slightly low of 99.99% at 773 K and 99.999% at 873 K and 973 K. There is no significant difference between the systems of potassium based salt and sodium based salt at high temperatures. The standard Gibbs energy change of decomposition in the sodium salt system is shown below.

\[ C_{12}H_{7}Cl_{3} (g) + 3 \text{NaOH (l)} + 13 \text{O}_2 (g) = 3 \text{NaCl (l)} + 5 \text{H}_2\text{O (g)} + 12 \text{CO}_2 (g) \dots \quad (7) \]
\[ \Delta G^o(\gamma) = -6 280 \text{kJ at } 673 \text{ K}^{20,21} \]
\[ \Delta G^o(\gamma) = -6 322 \text{kJ at } 973 \text{ K}^{20,21} \]
C_{12}HCl_3 (g) + 3/2 Na_2CO_3 (l) + 13 O_2 (g) = 3 NaCl (l) + 7/2 H_2O (g) + 27/2 CO_2 (g) ....... (8)

\[ \Delta G_{(8)}^0 = -6.024 \text{ kJ at } 673 \text{ K}^{20,21} \]
\[ \Delta G_{(8)}^{\circ} = -6.152 \text{ kJ at } 973 \text{ K}^{20,21} \]

From the viewpoint of thermodynamics, the driving force of decomposition in the potassium salt system is higher than that in the sodium salt system (see Eqs. (3) and (7) for comparison). However, no significant difference was observed experimentally between the two systems as previously described. This may be because the decomposition reaction is governed by the kinetic factor such as the transfer of reactants and products in the gas phase.

The decomposition efficiency of PCBs used in this study by using molten KOH-9.3 mol% K_2CO_3 is summarized in Fig. 11. The efficiency is the value on the average of 2-4 experiments. As shown in the figure, the decomposition efficiency increased with an increase of temperature, but there is no significant difference between 873 K and 973 K. This means that the dechlorination of PCBs was almost completed at 873 K. But the processing at higher temperature is required for the complete destruction of organic by-products. Through the whole experiments, no systematic change of the decomposition efficiency associated on the number of chlorine of PCBs was observed. This indicates that the decomposition of PCBs is governed by the kinetic factor and any PCB can be decomposed at similar level, which enables the treatment of multiple PCBs mixture.

The concentration of by-product chloride (KCl or NaCl) is increased with the progression of decomposition processing of PCBs. But the molten salts dissolve a large amount of the chloride and are kept in homogeneous liquid phase. As a simplified case, KOH melt dissolves KCl up to 74 mol% KCl (79 mass% KCl) in the two components system at 973 K.\(^{23}\) From the viewpoint of the driving force for the decomposition, Gibbs energy change of reaction (3) is described as follows.

\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{a_{KCl}^4 P_{H_2O}^5 P_{CO_2}^{12}}{P_{C_{12}H_7Cl_3} a_{KOH}^5 P_{O_2}} \right) \] ....... (9)

Fig. 11. Decomposition efficiency of PCBs by using molten salts with air. Average of 2-4 experiments is shown. Salt: KOH-9.3 mol% K_2CO_3, concentration of PCBs in solution: 2-20 mg (ml-nonane)\(^{-1}\), injection rate of solution: 5 ml·min\(^{-1}\), flow rate of imitation air: 60 ml·min\(^{-1}\), immersion depth of nozzle: 50 mm (mono-, di, tri, tetra), 75 mm (penta, haxa, hepta).

\[ \Delta G^0 = -6.374 \text{ kJ (mol-C}_{12}\text{H}_7\text{Cl}_3)^{-1} \text{ at } 973 \text{ K} .... (10) \]

The activity of KOH is decreased due to diluting with the by-product KCl. When the concentration of KOH decreased to 50 mol% in the mixed salt and the activity coefficient of KOH is assumed to be unity, the variation in the Gibbs energy change is calculated as follows.

\[-3RT \ln a_{KOH} = +16.8 \text{ kJ at } 973 \text{ K} .... (11)\]

This value is just 0.26% of \( \Delta G^0 \), which suggests that the driving force shows little change even though KOH is considerably diluted by KCl. From the viewpoint of mass transport, viscosities of KOH and KCl are 0.42 mPa·s and 1.36 mPa·s at 973 K, respectively. The viscosity of the mixed salt is slightly increased with increasing KCl concentration, but the salt has enough fluidity. Therefore, it is not considered that lowering of mass transport hinders the decomposition reaction. As discussed above, the decomposition ability of molten salt seems to be kept even though considerable amount of chloride is concentrated in the molten salt.

From the series of study, it was found that the decomposition efficiency of PCBs was drastically improved by using basic molten salts compared with simple incineration. This new process was also very effective for complete decomposition of PCBs containing multiple chlorine atoms. The features of the other representative decomposition processes for PCBs are summarized in Table 2 for comparison.

The most conventional incineration\(^{24,25}\) is available both for the dechlorination and decomposition of organic by-products at high reaction rate. However, the process temperature is high (over 1200°C), and the reactor becomes complicated in order to prevent the formation of dioxins in the exhaust during the cooling step. Our new process developed in this study is operated at lower temperature (600–700°C) in simple reactor because the chlorine in PCBs is extracted into molten salt and separated from the exhaust automatically.

The dechlorination by the reaction with metallic sodium suspension is a practical process used in Japan.\(^{26,27}\) This process has relatively simple reactor. However, the reaction rate is low and the organic residue after the dechlorination should be treated. Namely, multi-step treatment is required for the complete decomposition of PCBs. Our new process serves the one step treatment including both the dechlorination and decomposition of organic by-products. Furthermore, the reaction rate of the new process is significantly high.

The hydrothermal oxidation by using hot water or supercritical water is also used as a practical process in Japan.\(^{28-31}\) This process enables the one step treatment including both the dechlorination and decomposition of organic by-products at a relatively high reaction rate. But, this process should be carried out at a high pressure of 230–240 atm, and there is no practical reactor material due to the formation of hot concentrated hydrochloric acid solution as the by product. Therefore, a complicated reactor is needed. Our new process is carried out at an atmospheric pressure, and the handling and maintenance of the reactor is easy.

The reduction decomposition by using hydrogen gas\(^{32}\) and the decomposition by using ultraviolet light\(^{33}\) are also
studied as an alternative process in a laboratory scale, but the problem of complicated reactor or low reaction rate has not been solved.

Compared with above processes, the new process by using molten salts has high reaction rate and is available both for dechlorination and decomposition of organic by-products. The process requires a simple reactor and is operated under atmospheric pressure. The handling of dechlorinator (basic salt) is easy, and no toxic compounds such as dioxins are formed. Therefore, this process is hopeful for constructing a safe, efficient, and environmentally friendly waste treatment system of PCBs.

4. Conclusions

The decomposition of PCBs by means of basic molten salts was investigated. PCBs (mono, di, tri, tetra, penta, hexa, hepta-chlorophenylene) solution was injected into basic molten salts (KOH–K2CO3 or NaOH–Na2CO3) at 773–973 K with oxygen or imitation air. The residual mass of PCBs or the residual concentration of PCBs in the exhaust after the decomposition were determined by using GC-MS. The decomposition efficiency of PCBs reached to very high of 99.999% in an optimum condition. Chlorine of PCBs was captured in basic molten salts, and organic compounds comprising chlorine was not emitted from the salts. Some by-products comprising benzene rings formed at 773–873 K, but the by-products disappeared at 973 K.

Acknowledgement

The authors are grateful to Emeritus Professor Syuukuji Aasakura of the Yokohama National University for his valuable discussions throughout this project. This work was financially supported by a Grant-in-Aid for Scientific Research (A) (No. 15206082) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

REFERENCES

26) Y. Yukio and T. Otaka: Japan Patent, P2002-187858A.

Table 2. Comparison of decomposition processes for PCBs.

<table>
<thead>
<tr>
<th>Name of process</th>
<th>Process temperature</th>
<th>Pressure</th>
<th>Dechlorination</th>
<th>Decomposition of organic by-products</th>
<th>Reaction rate</th>
<th>Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incineration21,24</td>
<td>&gt; 1 200°C</td>
<td>Atmospheric pressure</td>
<td>○</td>
<td>○</td>
<td>High</td>
<td>Complicated</td>
</tr>
<tr>
<td>Sodium suspension25,26</td>
<td>≈ 90°C</td>
<td>Atmospheric pressure</td>
<td>○</td>
<td>○</td>
<td>Relatively high</td>
<td>Complicated</td>
</tr>
<tr>
<td>Hydrothermal oxidation27–30</td>
<td>380–410°C</td>
<td>230–240 atm</td>
<td>×</td>
<td>○</td>
<td>Relatively slow</td>
<td>Complicated</td>
</tr>
<tr>
<td>H2 reduction31</td>
<td>&gt; 850°C</td>
<td>Atmospheric pressure</td>
<td>○</td>
<td>○</td>
<td>High</td>
<td>Complicated</td>
</tr>
<tr>
<td>UV/catalyst32</td>
<td>50–75°C</td>
<td>Atmospheric pressure</td>
<td>○</td>
<td>○</td>
<td>Very high</td>
<td>Simple</td>
</tr>
<tr>
<td>This study (basic molten salts)</td>
<td>600–700°C</td>
<td>Atmospheric pressure</td>
<td>○</td>
<td>○</td>
<td>Very high</td>
<td>Simple</td>
</tr>
</tbody>
</table>