

## PC1) Decomposition of PVC and Ion exchange resin in supercritical water

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### 1. Introduction

In general, chlorinated organic substances including PCB and dioxins are stable to heat and thus hard to decompose. Polyvinyl Chloride(PVC), a chlorinated organic substance, is not harmful itself but it produces highly toxic material like dioxin during decomposition[1].

Disposal of PVC is more difficult than other plastics. As 57wt% of its molecules is chlorine, it produces large amount of hydrogen chloride during incineration, and as a result the incinerator can be easily damaged. And the chlorine reacts with the additionally produced organic ring compounds and produces dioxins[3-6].

In addition, disposables, paper, masks, and rubber gloves used in nuclear facilities are contaminated with low level radioactivity and cannot be simply discarded. Plastics used in nuclear power generation facilities contain a lot of incombustible material such as PVC. This makes the incineration and reduction of low level radioactive wastes very difficult.

Like polyethylene(PE), PVC[(CH<sub>2</sub>CHCl)<sub>n</sub>] is difficult to decompose with supercritical water only. PVC is more dangerous than PE because it produces hydrogen chloride at temperatures above 190°C[7]. If strong acid is generated in supercritical water, the reactor becomes corroded. In addition, PVC molecules form conjugated polyene, which increases double bonds in the molecules and makes PVC more difficult to decompose than PE.

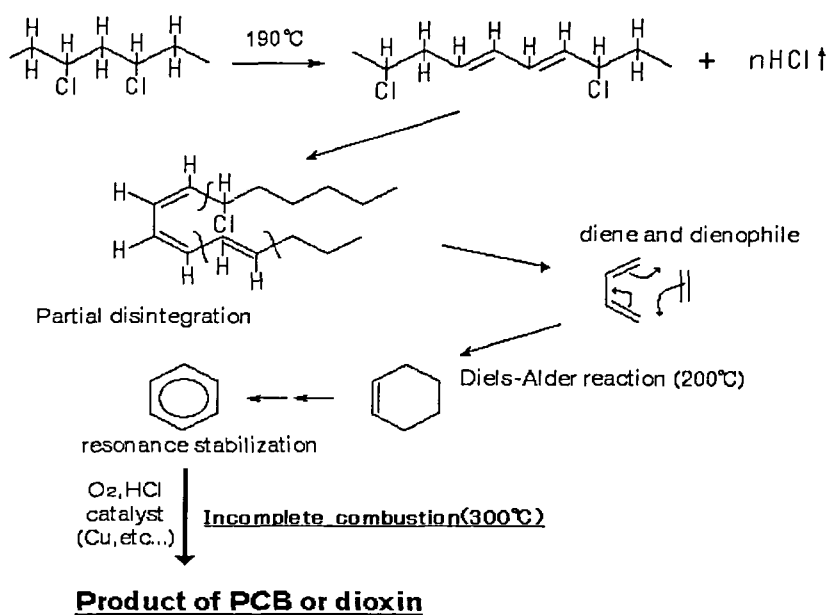


Fig. 1. Generating process of PCB or Dioxin for vice product of PVC combustion.

## 2. Chemicals and Experiment

The reactor used is made of corrosion resistant INCONEL625(Ni60%, Cr20%, Mo10%, Fe, Ni, Ta) alloy and its volume is 10.8ml. 150mg of each organic substance was treated in supercritical water and its decomposition rate was examined. Sodium nitrate as an oxidizer was used by n times the weight of organic substance. Here, n differs from experiment to experiment. Along with the sample, 3ml of water was injected into the reactor. Then, a rod heater was connected to the reactor to raise temperature. The reaction temperature was 450°C for all samples. After reaching 450°C, the temperature was maintained for 30 minutes. Then, the heater was turned off and the reactor was cooled naturally for 3 hours. Fig. 2 shows the cross sectional view of the reactor.

powder X-ray diffractometer(RINT2200V/PC-SV manufactured by RIGAKU). Then the JADE standard diffraction pattern data was referenced for the identification of the salt formed.

④The gas generated was analyzed. After putting the sample in the reactor, a valve was connected and the content of the reactor was substituted with Ar or He. For the analysis of gas components, GCMS QP5000, a gas chromatography mass spectrometry (GC-MS), manufactured by Shimadzu was used, and for the analysis of the amount of gas generated, TCP-GC8APT and FID-GC8APT manufactured by Shimadzu were used.

### 3. Results and discussion

#### 3.1. Time taken to reach the reaction temperature and exothermic reaction

The reaction temperature was 450°C. The supercritical temperature(373°C) was reached 17 minutes after applying heat. Fig. 3 is a graph showing the time and temperature change when PVC was treated in supercritical water. As can be seen in Fig. 3, the actual reaction time was around 30 minutes after applying heat. Heat was applied additionally for about 10 minutes after reaching the supercritical temperature(374°C). From Fig. 3, it can be seen that the reaction temperature exceeded the heating temperature after about 9 minutes. From this, it can be confirmed that supercritical water oxidation is an exothermic reaction as it is a combustion reaction of organic material.

In supercritical water oxidation, generally 1~10wt% of organic material is used per solvent. It is because if the concentration of organic substance is too high, the heat becomes too high and external cooling facility becomes necessary, which increases cost. For this experiment, the concentration of organic substance was 20wt%, but the experiment was carried out at temperatures lower than the supercritical water oxidation temperature(600~650°C), thus it caused less stress to the reactor.

The higher the amount of organic substance treated per solvent, the more efficient the method. But it is necessary to find the optimum amount taking into account the amount of exotherm.

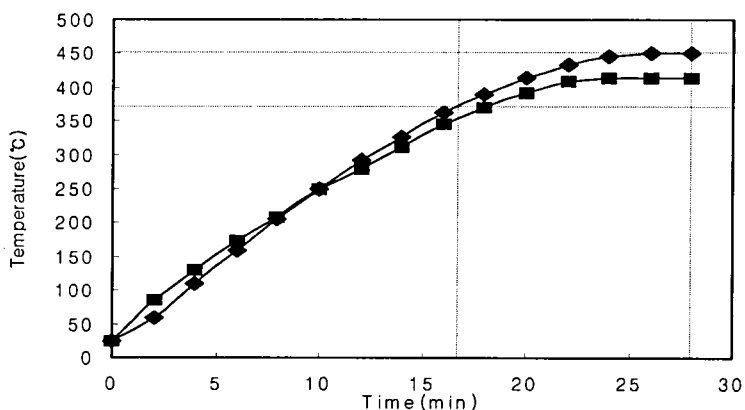


Fig. 2. Dependence of temperature by time of batch reactor system when PVC was treated in supercritical water. Reaction temperature(450°C), ◆:Temperature in reaction vessel.;■:Heater temperature.

#### 4. Abstract

This experiment was carried out at 450°C, which is relatively lower than the temperature for supercritical water oxidation (600–650°C). In this experiment, the decomposition rates of various incombustible organic substances were very high. In addition, it was confirmed that hetero atoms existed in organic compounds and chlorine was neutralized by sodium (salt formation).

However, to raise the decomposition rate, relatively large amount of sodium nitrate (3–4 times the equivalent weight) was required. When complete oxidation is intended as in the case with PCB, the amount of oxidizer and decomposition cost is important. But when vaporization reduction is required as in the case with nuclear wastes, the amount of radioactive wastes increases instead.

But as can be seen in the result of XRD measurement, unreacted sodium nitrate remained unchanged. If oxidation reaction of organic substance simply depends on collision frequency, unreacted sodium nitrate can be recovered and reused, then oxidation equivalent weight would be sufficient.

In the gas generated, toxic gas was not found. As the supercritical water medium has high reactivity, it is difficult to generate relatively low energy level SO<sub>x</sub> and NO<sub>x</sub>.

**keywords** : Polyvinyl Chloride(PVC); Ion exchange resin; Supercritical water; Oxidation; Nitrate; Nitrite.

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