Hydrothermal decomposition of pentachlorophenol in subcritical and supercritical water with sodium hydroxide addition

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Abstract

Hydrothermal decomposition of pentachlorophenol (PCP, C_6HCl_5O), as the probable human carcinogen, was investigated in a tubular reactor under subcritical and supercritical water with sodium hydroxide (NaOH) addition. The experiments were conducted at a temperature range of 300–420°C and a fixed pressure of 25 MPa, with a residence time that ranged from 10 s to 70 s. Under the reaction conditions, the initial PCP concentrations were varied from 0.25 to 1.39 mmol/L and the NaOH concentrations were varied from 2.5 to 25 times of the concentrations of PCP. The result of this study showed that PCP conversion in supercritical water was highly dependent on the reaction temperature, residence time, and NaOH concentration. PCP conversion in subcritical water is, however, only dependent on reaction temperature. NaOH concentration and residence times were found to have little effect on PCP conversion in subcritical condition. It was found that NaOH concentration affected the dechlorinations of PCP in the supercritical water. The intermediates detected were proposed to be tetrachlorophenol and trichlorophenol, respectively.

Key words: pentachlorophenol; hydrothermal decomposition; supercritical water; subcritical water

Introduction

Pentachlorophenol (PCP) was one of the most widely used biocides in the United States. It was registered for use by Environmental Protection Agency (EPA) as an insecticide, fungicide, herbicide, molluscicide, algae-cide, anti-microbial agent, disinfectant, wood preservative (ATSDR, 2001), and also for adhesives, latex paints, paper coatings, coatings in reusable bulk food storage containers, photographic solutions, leather tanneries, pulp, and paper mills (Brett, 1991). Given the widespread use of PCP, the finding of PCP constitute as a common organic waste materials is not surprising, which require disposal or destruction. Disposal has usually achieved in landfills or incineration, but this practice will rapidly become quite expensive and very restricting. Among the alternatives practices, hydrothermal oxidation is being investigated as a method for destroying liquid wastes and sludge. End products resulting from hydrothermal conversion are essentially water and mineral acids in liquid phase and carbon dioxide, molecular nitrogen in gas phase (Schmieder and Abeln, 1999; Weingartner and Franck, 2005).

For the past decade, pure water at high temperature, both sub- and super-critical water, has been growing importance as a medium for chemical reaction, primarily for the oxidation of hazardous chemical wastes (Akiya and Savage, 2002; Barner et al., 1992; Fang et al., 2005; Katritzky et al., 1996; Shaw and Dahmen, 2000; Veriansyah et al., 2005, 2006a, 2006b, 2006c, 2006d). Although the sub- and superc-ritical water have been successfully used as a medium to treat a wide range of hazardous chemical waste to an acceptable destruction levels, the non-oxidation reactive behavior of much hazardous materials in sub- and super-critical water has not yet fully understanding. The present study examines the hydrothermal decomposition of PCP in sub- and super-critical water with sodium hydroxide addition. The primary goal of our work was to characterize the conversion of PCP in sub- and super-critical water. Thus, we explored factors that systematically affected the conversion of PCP, such as reaction temperature, residence time, and sodium concentrations. This study will then contribute to the collective knowledge of non-oxidation reactive behavior of PCP for the development of future sub- and super-critical water process.

1 Materials and methods

1.1 Apparatus and procedure

The experiments were conducted in a laboratory-scale, continuous-flow reactor system. A schematic diagram of the system for hydrothermal decomposition experimental apparatus is shown in Fig.1. All wetted parts, from the high pressure pumps to the gas-liquid separator, were made of stainless steel 316 (SS316) except that the
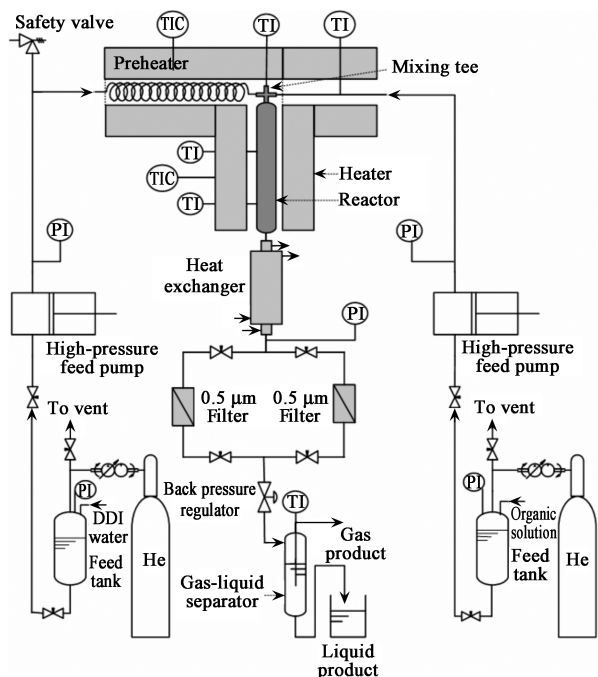
Fig. 1 Schematic diagram of the continuous-flow reactor system for hydrothermal decomposition experiments.

reactor was constructed from a 280-mm length of 18 mm outer diameter (O.D.) and 9.5 mm inside diameter (I.D.) stainless steel 304 tubing. The system involves two parallel sets of equipment that are almost identical: one for delivering the PCP solution and the other for the distilled and deionized (DDI) water. The two feed streams were pressurized in two different lines by two high-pressure pumps (Thermo Separation Product Company) and then separately preheated. The DDI water was preheated in a 6-m of 1/8 in 3.175 mm (O.D.) tubing, meanwhile the wastewater feed stream was preheated by flowing through a 0.5-m of 1/8 in O.D. tubing. After preheating, two lines were mixed at the reactor inlet using a SS316 mixing tee. Upon exiting the reactor, the effluent was cooled rapidly by passing through a shell and tube heat exchanger and afterwards, it was filtered to separate the solid particles by a 0.5-μm inline metal filter before it was depressurized to ambient condition by a back-pressure regulator (Tescom Co., model 26-1721-24). The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder, and their volumetric flow rate was determined by measuring the time interval.

1.2 Materials and analytical methods

Pentachlorophenol (PCP) feed was prepared by making an aqueous solution of PCP (Aldrich, 98% purity) with sodium hydroxide (Junsei Chemical Company, 93% purity) which was used as received and dissolved in DDI water. The electrical resistance of the DDI water used in all experimental and analytical processes was approximately 18 MΩ. All the standard solutions for calibration in liquid analytical methods were prepared using high purity chemicals (Aldrich, ACS grade).

PCP concentrations in both feed and effluent liquid phase were determined by reverse-phase high-performance

liquid chromatography (HPLC) on a Symmetry C-8 of 5 μm column (3.9 mm × 150 mm, Waters Associated, Milford, USA). The HPLC system was equipped with a solvent delivery pump (Young Lin M930) and UV absorbance detector (Young Lin M720). Elution was performed at a flow rate of 1.2 ml/min using the mobile phase gradient 60/40 of acetonitrile/water with 1% acetic acid. The absorbance was monitored at 300 nm. PCP conversion, X, was calculated as follows:

$$X = 1 - \frac{C_{PCP_f}}{C_{PCP_i}} \tag{1}$$

where, C_{PCP_f} and C_{PCP_i} are the concentrations at the reactor inlet and outlet, respectively. Ion chromatography (Dionex DX-100) was used to determine concentration of chloride ions in the effluent. The system was equipped with an anion column (IonPac-AS14) and an anion self-regenerating suppressor (ASRS-Ultra II). The signal output was recorded using a Hitachi integrator (model D-2500). Identification of the reaction products was performed by a gas chromatography mass spectroscopy (Pegasus III GC-ToFMS) of the liquid effluent (after extraction in dichloromethane).

2 Results and discussion

The hydrothermal decomposition experiments were conducted in an isothermal and isobaric flow reactor in the absence of oxygen. The range of conditions explored for these experiments is presented in Table 1. The initial PCP and NaOH concentration is the concentrations at the reactor entrance, as described in previous published work (Veriansyah *et al.*, 2006c). For consistency with all previous experiments conducted at our laboratory, a nominal operating pressure of 25 MPa was selected. This pressure is far enough above its critical pressure so that the physical properties of water (e.g., density, dielectric constant) are not affected by small pressure fluctuations (Veriansyah *et al.*, 2006d). The reaction products included gaseous and liquid components. Since the amount of gas produced in the reaction was too low to measure, it was difficult to determine quantitatively and qualitatively. Thus, gas analyses were excluded in these experiments.

The effects of reaction temperature and residence time on PCP conversion were determined by a series of experiments in which residence time and reaction temperature

Table 1 Experimental conditions for PCP hydrothermal decomposition

Experimental variable	Range of value
Pressure (MPa)	25
Temperature (°C)	300–420
Residence time (s)	10–70
Initial pentachlorophenol (PCP) concentration[a] (mmol/L)	0.25–1.39
Initial sodium hydroxide (NaOH) concentration[a] (mmol/L)	0.62–34.87
Molar [NaOH]/[PCP] ratio	2.5–25

[a] PCP and NaOH concentration at the reactor inlet was calculated from the feedstock concentration and flow rates of the feed streams with the process condition.

were changed while the other parameters were kept constant. Fig.2 presents the resulting conversion of PCP as a function of the temperature and residence time measured in the hydrothermal decomposition experiments. As shown in Fig.2, the conversion of PCP at subcritical and supercritical water was increased with increasing the reaction temperature. The conversion of PCP was measured to be 25.5% at reaction temperature of 300°C and residence time 20 s. An additional 12.5% conversion was obtained for a total conversion of 38.0% at 350°C. For the conversion of PCP in supercritical water, it was measured to be 53.7% under conditions of residence time 20 s and reaction temperature 380°C. As the temperature increased, additional conversion of 46.2% was obtained for a total conversion of 99.9% at 420°C. This documents that PCP

were decomposed as the reaction temperature increased. The results of the experiments to examine the effect of residence time on PCP conversion shown in Fig.2 reveal that only slight changes of PCP conversion were observed with changes in residence time in subcritical water. On the contrary, increasing the residence time enhances the PCP conversion in supercritical water.

The influence of the NaOH concentration on the PCP conversion was determined by conducting twenty experiments at five variation temperatures and fixed residence times of 30 s and pressure of 25 MPa. Fig.3 shows that the conversion of PCP in supercritical water was increased with increasing the NaOH concentration. For the conversion of PCP in subcritical water, only slight changes were observed with changes in NaOH concentration. This shows that the decomposition of PCP is promoted by NaOH addition in supercritical water but not in subcritical water. NaOH concentration also affected the dechlorinations of PCP in the supercritical water as it was monitored in this study. At 380°C, 19.8% chloride ion dissociated at molar [NaOH]/[PCP] ratios of 2.5, as the molar ratios is increased, additional chloride ion dissociated of 61.9% was obtained for a total chloride ion dissociated of 81.7% at molar ratios of 25.

In the effluent of PCP hydrothermal decomposition with NaOH addition in supercritical water, intermediate products were detected. Fig.4 shows an example of total ion chromatograms of effluents, which was obtained at 380°C, 25 MPa, 30 s of residence time, and molar [NaOH]/[PCP] ratios of 10. The structures given in Fig.4 indicate the results of the computer match to those of mass spectra. Intermediates detected were proposed to be tetrachlorophenol and trichlorophenol. These intermediates inferred that the removal of chlorine in PCP might proceed via an intermediate composed of an ion-dipole bond between sodium cations and chlorine in PCP, as shown in Fig.5, and generally agree with Lee *et al.* (2002), experimental results for the effect of a sodium hydroxide addition on the decomposition of 2-chlorophenol in supercritical water. Since these intermediates products could be harmful to human health and environment, a further process would be required to degrade these products.

3 Conclusions

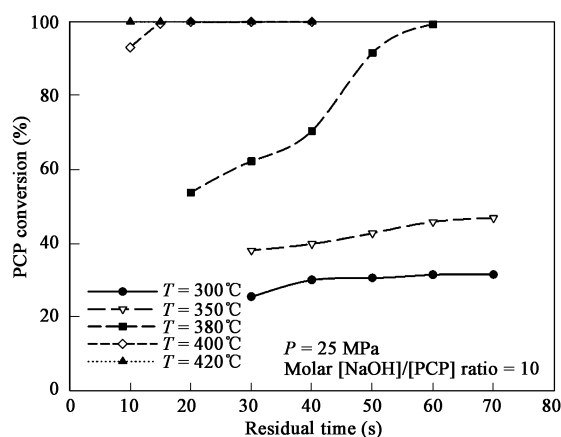The hydrothermal decomposition of PCP was investigated under subcritical and supercritical water with NaOH

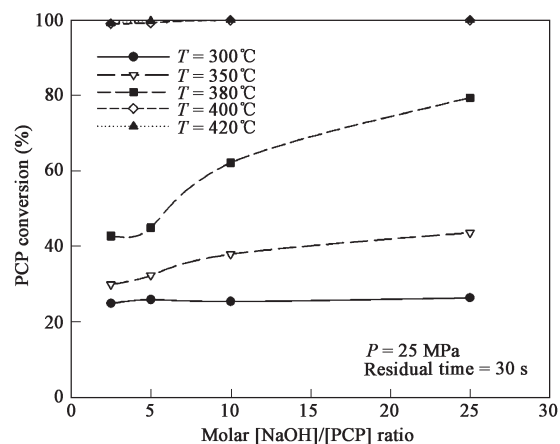Fig. 2 Effect of temperature and residence time on PCP conversion.

Fig. 3 Effect of molar [NaOH]/[PCP] ratios on PCP conversion.

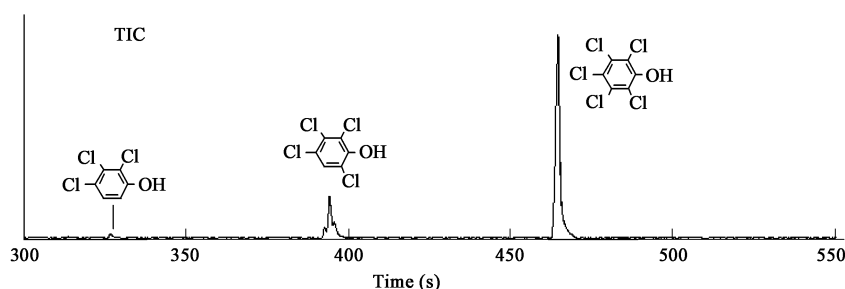Fig. 4 Total ion chromatogram of PCP decomposition products at 380°C and 10 molar [NaOH]/[PCP] ratio.
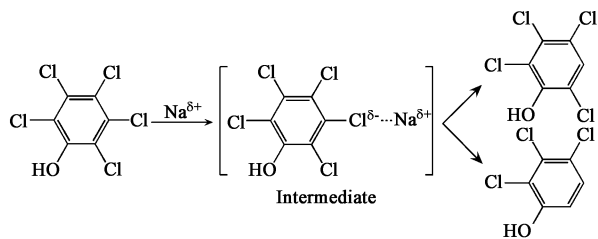
Fig. 5 Possible reaction pathway of Cl abstraction from PCP by sodium cations in supercritical water.

addition at residence times of 10–70 s and a fixed pressure of 25 MPa. The results showed that PCP conversion in supercritical water is highly dependent on the reaction temperature, residence times, and NaOH concentration. PCP conversion at subcritical water is, however, only dependent on reaction temperature. NaOH concentration and residence times were found to have little effect on PCP conversion in subcritical condition. It was found that NaOH concentration affected the dechlorinations of PCP in the supercritical water. The removal of chlorine in PCP might proceed via an intermediate composed of an ion-dipole bond between sodium cations and chlorine in PCP. GC/MS analysis of the effluent gave identification of intermediates such as tetrachlorophenol and trichlorophenol which could be harmful to human health and environment. Thus, a further treatment process is required to degrade the intermediate products of the hydrothermal decomposition.

Acknowledgements

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