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Kinetic Analysis for Decomposition of 2,4-Dichlorophenol by Supercritical Water Oxidation

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Abstract−2,4-Dichlorophenol (2,4-DCP), as a halogenated model pollutant, was decomposed by using supercritical water oxidation (SCWO) in a batch reactor made of Hastelloy C-276. SCWO experiments for 2,4-DCP decomposition were performed in the range of 380-420 °C, 230-280 bar and 0.074-0.221 mol/L H_2O_2. The effect of oxidant concentration on decomposition rate and efficiency was significant near the critical temperature of 380 °C. However, the role of the oxidant concentration in the SCWO process decreased with an increase in temperature; also, excess oxidant played a key role in quite significantly decreasing the activation energy of 2,4-DCP oxidation. Variation of the reaction rate by the change of pressure was negligible even at a near critical temperature. The kinetic rate for the decomposition of 2,4-DCP in the SCWO process was well described by a simple first-order kinetic and global reaction rate model. From the SCWO experiments, the various intermediates identified with a GC/MS implied that the first reaction pathway for 2,4-DCP decomposition led to dimers such as dichlorophenoxyphenols, and the second led to single-ring and ring-opening products.

Key words: 2,4-Dichlorophenol (2,4-DCP), Supercritical Water Oxidation (SCWO), Kinetic Rate

INTRODUCTION

Chlorinated phenols are significantly harmful environmental pollutants because of their high toxicity, recalcitrance, bioaccumulation, strong odor emission, persistence in the environment and suspected carcinogenicity and mutagenicity. They are the result of a range of man-made activities, such as the production of wood preservers, pesticides and biocides [Armenante et al., 1999].

Several different methods, both physical and chemical, have been used to remove phenols and their derivatives from wastewater, such as adsorption over activated carbon, air stripping, chemical oxidation, solvent extraction, ultraviolet light, ozone, etc. Unfortunately, high cost and low process efficiency limit their application [Cocero et al., 2002].

The supercritical water oxidation (SCWO) process was introduced for the decomposition of chemically stable compounds such as dioxin, chlorinated hydrocarbons and others [Sako et al., 1997; Lee et al., 2002]. Hazardous organic compounds are completely oxidized and converted to carbon dioxide (CO_2) and water (H_2O) by using either oxygen, hydrogen peroxide or air as an oxidant above the critical point of water (T_c=374 °C, P_c=221 bar) [Peter and Eckhard, 2001]. In general, the desired decomposition and removal efficiency by way of SCWO can be achieved in a few seconds or minutes [Sako et al., 1997; Peter and Eckhard, 2001; Lee et al., 2002].

The properties of water, such as density, viscosity, diffusivity and its static dielectric constant, are changed dramatically by slight variations of temperature and pressure at the near critical point. In addition, the static dielectric constant of supercritical water (SCW) is close to that of non-polar solvents because of its minuscule value (supercritical condition<2, atmospheric condition≈80) [Modell, 1986; Konys et al., 1999]. And hydrogen bonding decreases with a decrease in water density [Uematsu et al., 1980; Mitton et al., 2000]. Therefore, since organic compounds and gases become miscible in the SCW process, reaction can occur in a single phase, and mass transfer resistance becomes negligible [Connoly, 1966; Japas and Frnack, 1985].

SCWO is an effective technique for the treatment of toxic and refractory compounds, but it needs to take into account both corrosion due to acid and fouling due to the low solubility of inorganic salts before it can be successfully applied to halogenated compounds [Kritzer et al., 1998; Peter and Eckhard, 2001]. Therefore, knowing the reaction kinetics of halogenated compounds under SCW conditions is essential for the design and development of SCWO processes. A global reaction model has been extensively used to analyze the SCWO process [Gopalan and Savage, 1995; Lin et al., 1999; Motonobu et al., 1999; Matsumura et al., 2000] and, a generalized kinetic model has been developed to account for the rate controlling intermediates in the reaction mechanism [Ruokang et al., 1993].

The purpose of this study was to discover the decomposition kinetics of 2,4-dichlorophenol (2,4-DCP) by using SCWO. Due to stainless steel's durability and corrosion resistance at a high temperature and pressure when an oxidant is used, a batch reactor of Hastelloy C-276 was made that was more inert than ordinary stainless steel. The decomposition of 2,4-DCP was experimented at the near critical range of water (380-420 °C and 230-280 bar) with the batch reactor. In addition, the decomposition efficiency of 2,4-DCP was analyzed by using varying amounts of hydrogen peroxide (H_2O_2). From the results, a single first-order kinetic model was

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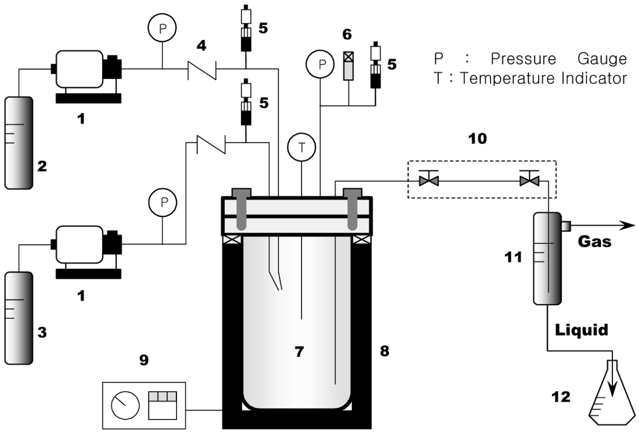

Fig. 1. Schematic diagram of experimental apparatus for supercritical water oxidation.

1. High pressure pump
2. Water tank
3. Oxidant tank
4. Check valve
5. Pressure transducer
6. Relief valve
7. Reactor
8. Heater
9. Heat controller
10. Sample loop
11. Air/water separator
12. Sample tray

proposed and reaction intermediates in the SCWO process presented.

EXPERIMENTAL SECTION

1. Materials

2,4-Dichlorophenol (2,4-DCP, $C_6H_4Cl_2O$, 99% purity) was purchased from Acros Organics Co. Ltd. Once 2,4-DCP was dissolved in secondary purified water, the solution was used as a feed for the SCWO experiments. Hydrogen peroxide (H_2O_2, 30 wt% purity, Junsei Chemical Co. Ltd.) was used as an oxidant.

2. Apparatus and Procedure

The SCWO experiments with 2,4-DCP were conducted in a high-pressure batch reactor. A schematic diagram of experimental apparatus for the decomposition of 2,4-DCP under SCW conditions is shown in Fig. 1. The experimental system consists of two high pressure syringe pumps (Lab alliance prep. 100, P_{max}=408 bar) - used to feed the solution (2,4-DCP) and oxidant (H_2O_2), a reactor, and a pressure relief valve (Parker, USA). It was known that Ni-based alloys (Hastelloy C-276, C-22, G-30 and Inconel 625) and Fe-based duplex steel (Ferralium 255) show more resistance to corrosion than Fe-based steel (Stainless steel 316) [Mitton et al., 2000]. Therefore, in this study, a cylindrical-type reactor was made of Hastelloy C-276 with a volume of 588 cm^3. Except for the reactor body, everything was connected with high pressure stainless steel 316 tubes and fittings. Tubes and fittings were installed in the reactor as close as possible to minimize the dead volume (Inside diameters of tube were 1/4", 1/8" and 1/16" with lengths of 3.87, 1.375 and 0.787 mm, respectively). An electrical heater was installed in the reactor to maintain temperature. A K-type thermocouple, located inside the reactor, was used to measure reactor temperature. Pressure was measured with a pressure gauge and pressure transducer. A relief valve was installed in the reactor in case of a temporary rise in pressure or in the event of corrosion.

Measured 2,4-DCP solution was fed onto the reactor and heated up to the desired temperature. Then hydrogen peroxide was rapidly injected into the reactor via the tube supplying the oxidant (0.787 mm I.D.) using a high-pressure syringe pump. The volume of the tube was set to minimize error in the amount of hydrogen peroxide supplied. In order to study the effect of oxygen concentration on decomposition efficiency, the concentration of hydrogen peroxide was changed from 0.074 to 0.221 mol/L. Since the supplied mixture had to be stable in the reactor, a sample was collected 20 seconds after the oxidant was introduced. The sample was cooled instantly in a sample loop that consisted of two high-pressure valves and tube (1/4" O.D., 3.87 mm I.D.). It was then depressurized to atmospheric pressure through a phase separator. Finally, approximately 2 mL of this sample was collected in a sampling vessel.

3. Sample Analysis

A GC/FID (5980 series 2, HP) with a capillary column (HP-1) was used to analyze decomposition efficiency. The oven operating temperature was set at 150 °C and the injection temperature was set at 300 °C. Helium was used as a carrier gas at a 1 ml/min flow rate. The intermediate species in the liquid sample were analyzed by a GC/MS (HP 5890/LECO Pegasus III) with the MS-Range from 30 to 500 amu. The MS analyses were carried out in SCAN mode using electron impact ionization (EI, 70 eV). For GC/MS analysis, a 5 mL of dichloromethane (GR grade, Junsei Chemical Co., Ltd.) was used to extract organic products from the 5 mL aqueous sample, acidified at about pH 2. Extraction was repeated twice. The GC/MS computer library was used to identify the products, with a match >90 (100 the maximum) considered as the minimum requirement for the positive identification of intermediates. The retention time of the product was also compared with that of an authentic compound.

RESULTS AND DISCUSSION

1. Decomposition Efficiency

Before the SCWO experiments, the extent of the thermal degra-

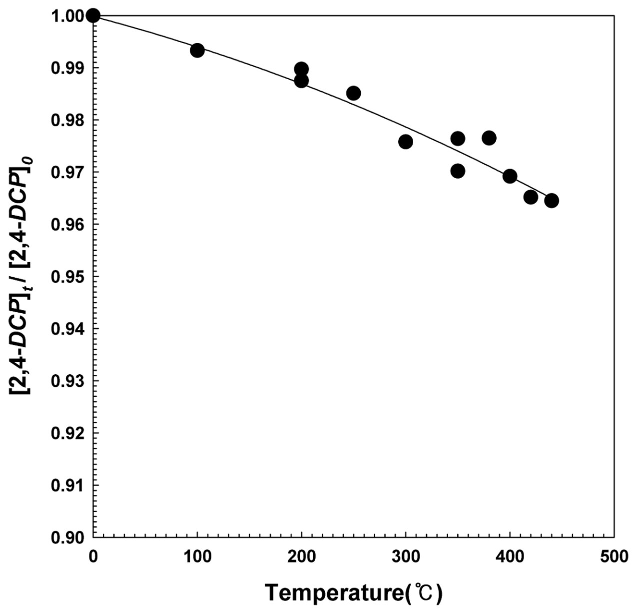

Fig. 2. Thermal decomposition of 2,4-DCP with temperature.

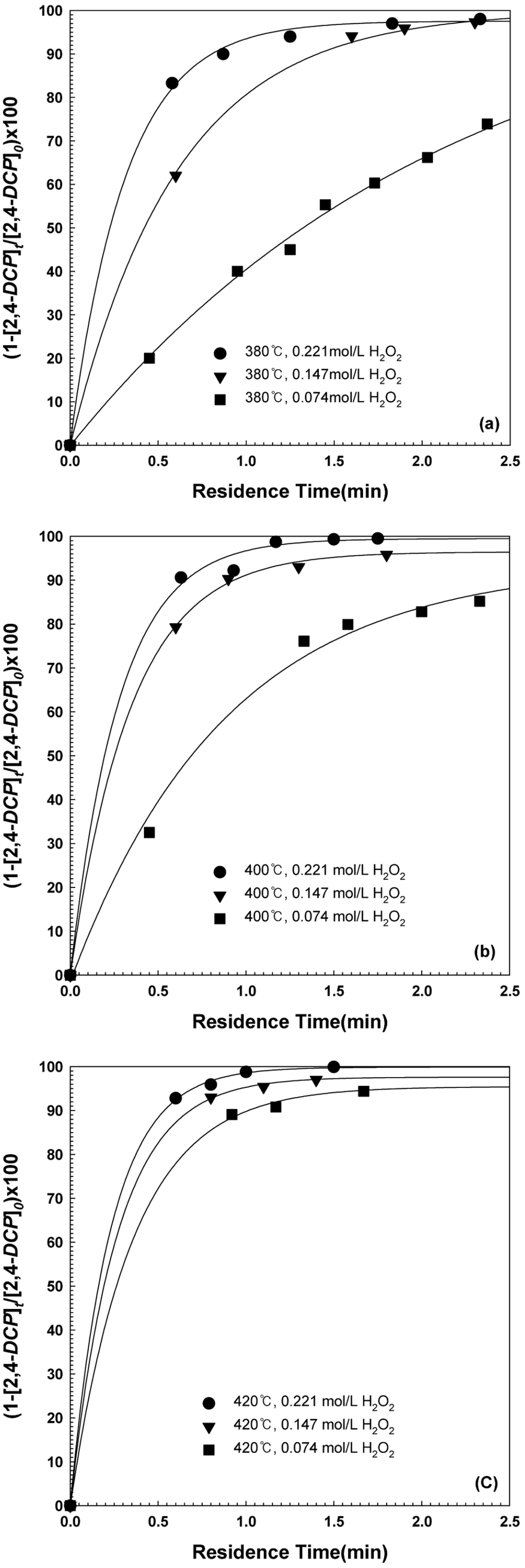

Fig. 3. Decomposition efficiencies of 2,4-DCP with oxidant (0.074, 0.147 and 0.221 mol/L H_2O_2), temperature ((a) 380 °C, (b) 400 °C and (c) 420 °C) and residence time at 230 bar.

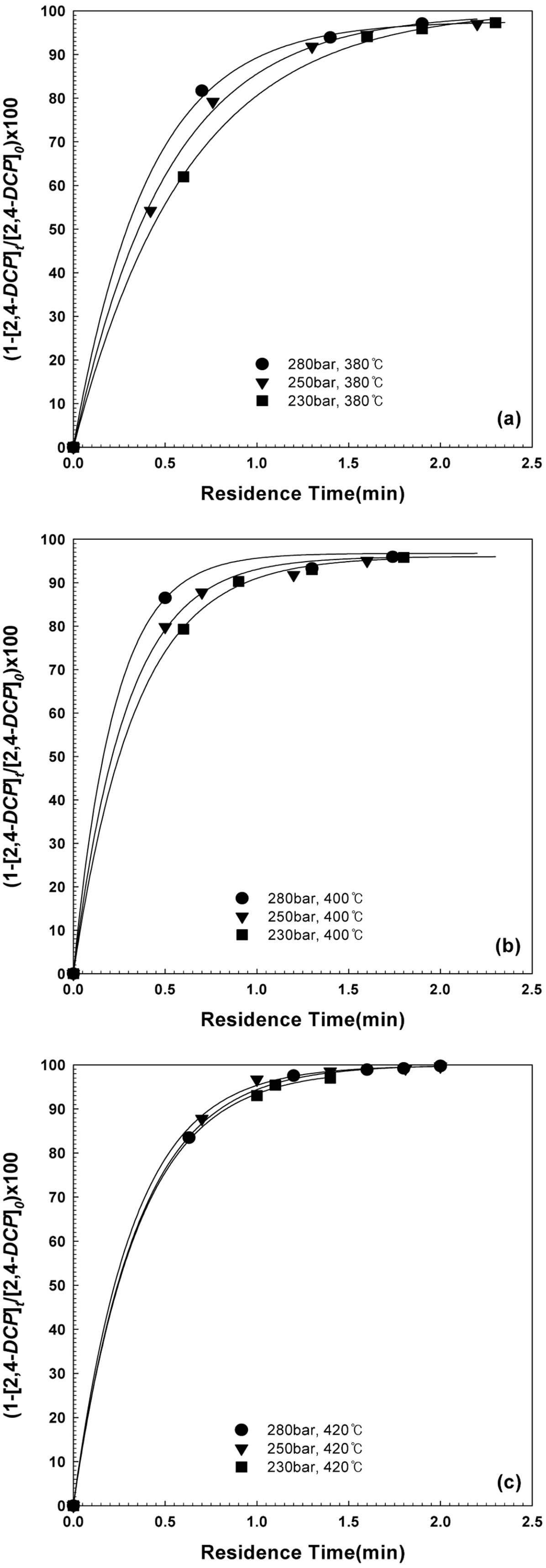

Fig. 4. Decomposition efficiencies of 2,4-DCP with pressure (230, 250 and 280 bar), temperature ((a) 380 °C, (b) 400 °C and (c) 420 °C) and residence time at 0.147 mol/L H_2O_2.

Table 1. Decomposition of 2,4-DCP under various conditions

Temperature (°C)	Pressure (bar)	Residence time (s)	2,4-DCP Concentration* (mol/L)	H_2O_2 concentration (mol/L)	Decomposition efficiency (%)
380(±1)	230(±1)	27.0-142.2	5.990×10^{-3}	0.074	20.0-76.9
380(±1)	230(±1)	36.0-138.0	5.990×10^{-3}	0.147	62.0-97.3
380(±1)	230(±1)	34.8-139.8	5.990×10^{-3}	0.221	83.3-98.0
380(±1)	250(±1)	25.2-144.0	5.990×10^{-3}	0.147	40.7-93.1
380(±1)	280(±1)	43.1-141.0	5.990×10^{-3}	0.147	72.7-92.1
400(±2)	230(±1)	27.0-139.8	5.945×10^{-3}	0.074	32.5-85.2
400(±2)	230(±1)	36.0-108.0	5.945×10^{-3}	0.147	79.3-95.8
400(±2)	230(±1)	37.8-105.0	5.945×10^{-3}	0.221	90.6-99.5
400(±2)	250(±1)	30.0-138.0	5.945×10^{-3}	0.147	79.8-98.1
400(±2)	280(±1)	30.0-132.0	5.945×10^{-3}	0.147	81.7-98.2
420(±2)	230(±1)	55.2-100.2	5.920×10^{-3}	0.074	89.1-94.4
420(±2)	230(±1)	48.0-84.0	5.920×10^{-3}	0.147	93.0-97.0
420(±2)	230(±1)	36.0-90.0	5.920×10^{-3}	0.221	92.8-99.99
420(±2)	250(±1)	36.0-120.0	5.920×10^{-3}	0.147	90.6-99.8
420(±2)	280(±1)	30.0-120.0	5.920×10^{-3}	0.147	86.5-99.8

*The initial feed concentration is 6.135×10^{-3} mol/L.

dation of 2,4-DCP during the heat-up period was investigated within the range of 100-440 °C without the addition of hydrogen peroxide. As shown in Fig. 2, 0.7-3.5% of the 2,4-DCP supplied decomposed with the increase of temperature at 230 bar. Since the feed solution was not degassed to eliminate dissolved oxygen, thermal degradation of 2,4-DCP can occur due to both hydrolysis and oxidation. Although the extent of thermal degradation was not significant in the SCWO experiments, it was considered in estimating the efficiency of 2,4-DCP decomposition.

Fig. 3 and Table 1 show the effect of temperature and H_2O_2 concentration in decomposing 2,4-DCP (6.135×10^{-3} mol/L of 2,4-DCP). The decomposition rate increased markedly with an increase in the temperature and concentration of H_2O_2. Decomposition efficiency approached 99.99% at 0.221 mol/L H_2O_2, 420 °C and 230 bar within 90 seconds.

As shown in Fig. 3(a), the effects of oxidant concentration on decomposition rate and efficiency were significant at the near critical temperature, 380 °C. However, the role of the oxidant concentration decreased with an increase in temperature, as in Figs. 3(b) and (c). This implies that SCWO at near critical temperature is significantly affected by additives because the physical properties of water are abruptly changed. In addition, we can see that complete oxidation of 2,4-DCP in the SCW could be obtained at a temperature near 420 °C while decomposition maximized at around 98% with other temperatures.

Fig. 4 shows the effect of pressure on the decomposition of 2,4-DCP with a constant concentration of hydrogen peroxide, 0.147 mol/L. Decomposition rate and efficiency at near critical temperature were affected by pressure, while performance differences among the pressure conditions were negligible at 420 °C. Moreover, compared with Fig. 3, the effect of pressure was much smaller than the effect of temperature with respect to decomposition rate and efficiency. This means that the increment of temperature is more efficient than that of pressure in terms of saving energy.

Fig. 5 shows a comparison of results for the decomposition of 2,4-DCP using SCWO and other processes. Published results show that the residence times for 2,4-DCP decomposition with regard to biological treatment (0.307×10^{-3} mol/L 2,4-DCP in SBR system) [Quan et al., 2003], photo assisted penton oxidation (2.779×10^{-3} mol/L 2,4-DCP) [Ormad et al., 2001] and photocatalyst oxidation with CdS (0.5×10^{-3} mol/L 2,4-DCP) (24) were 8 days, 54 min and 40 min, respectively. However, as shown in Fig. 5, the residence time for the SCWO based on 420 °C and 230 bar conditions (6.135×10^{-3} mol/L 2,4-DCP and 0.221 mol/L H_2O_2) was 1.5 min, and this was despite a higher concentration of 2,4-DCP. Therefore, a well designed SCWO process is more efficient than other processes from the point of view of the rate of oxidation.

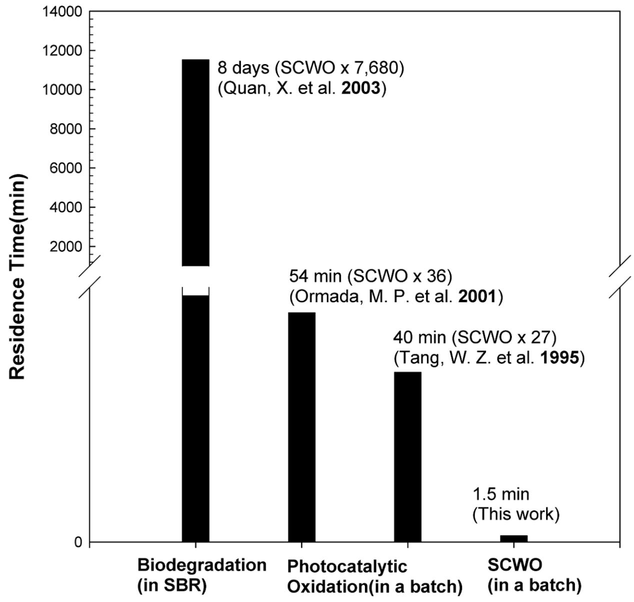

Fig. 5. Comparison between other processes and SCWO in this work based on over 99.99% decomposition of 2,4-DCP.

2. Reaction Kinetics

The reaction kinetics for the decomposition of 2,4-DCP using SCWO was studied. The decomposition yield for 2,4-DCP is defined as follows:

$$\text{Decomposition (X)} = 1 - \frac{[2,4\text{-DCP}]_t}{[2,4\text{-DCP}]_0} \tag{1}$$

where $[2,4\text{-DCP}]_0$ and $[2,4\text{-DCP}]_t$ are the influent and effluent concentrations of 2,4-DCP.

For engineering purposes, it is often sufficient to develop a global rate model to express the reduction of waste components in SCWO. Therefore, in the development of kinetic models, most researchers have adopted the global rate equation for the overall oxidation reaction [Ruokang et al., 1993; Martino and Savage et al., 1999; Jianli and Savage, 2000; Takehiro et al., 2000; Portela and Neot, 2001]. The following equation was applied for the decomposition rate of 2.4-DCP in the SCWO process using hydrogen peroxide:

$$\frac{-d[2,4\text{-DCP}]}{dt} = A\exp(-E_a/RT)[2,4\text{-DCP}]^a[H_2O_2]^b[H_2O]^c \tag{2}$$

where [2,4-DCP], $[H_2O_2]$ and $[H_2O]$ represent the concentration of each component (mol/L). The reaction order of 2,4-DCP, H_2O_2 and H_2O are presented by a, b and c, respectively. E_a, R, T and A are activation energy, gas constant, reaction temperature, and the Arrhenius pre-exponential factor, respectively.

Since a reaction rate constant can be defined by $k=A\exp(-E_a/RT)$, Eq. (2) can be reduced to the following:

$$\text{Rate}(r_{[2,4\text{-}DCP]}) = -\frac{d[2,4\text{-DCP}]}{dt} = k[2,4\text{-DCP}]^a[H_2O_2]^b[H_2O]^c \tag{3}$$

Water seems to participate in the reaction as a reactant via a multistep reaction mechanism. Since the reaction medium always consisted of more than 99% of water in this study, its impact on the 2,4-DCP disappearance rate, if any, may be hidden. In other words, the experiments were not designed to evaluate the effect of water concentration. In this way, we considered zero the reaction order for the water due to excess water [Lee et al., 2004; Cristopher et al., 1999; Jianli et al., 2000].

When τ is defined as residence time, Eq. (3) can be solved analytically with the initial condition x=0 at $\tau=0$ to clarify the relationship between 2,4-DCP and relevant process variables.

$$(1-x)^{1-a} - 1 = (a-1)k[2,4\text{-DCP}]_0^{a-1}[H_2O_2]_0^b\tau, \qquad \text{if } a\neq 1 \tag{4}$$

$$\ln(1-x) = -k[H_2O_2]_0^b\tau, \qquad \text{if } a=1 \tag{5}$$

We used a nonlinear regression analysis to fit the experimental 2,4-DCP conversions in Table 1 to Eq. (4) and thereby determine optimized values for the parameters a, b, A and E_a. The objective function minimized in the regression method was the sum of the squares of the differences between the values of x calculated from Eq. (3) and those measured experimentally. From nonlinear regression, the pre-exponential (A) and energy activation (E_a) value are simultaneously obtained. In this study, to obtain four reasonable parameters (a, b, A and E_a) from the nonlinear regression, the initial value of each parameter was evaluated. At first, after the value of k was fixed by using the reference value [Lee et al., 2005; Jianli et al., 2000; Ruokang et al., 1993], the values of reaction orders were optimized. Then, the rate constant, k, using the obtained reaction orders was evaluated at each experimental condition. By using these values, the activation energy, which varied in the amount of the supplied oxidant, was obtained from the Arrhenius plot. Finally, the average value of each parameter was used as the initial value in the nonlinear regression analysis [Lee et al., 2005]. The optimal values of the kinetic parameters lead to the global rate law of Eq. (6) to describe 2,4-DCP oxidation.

$$\text{Rate} = (1.69\pm0.72)\times10^3\times\exp\left(-\frac{58{,}370\pm15{,}160}{RT}\right) \times[2,4\text{-DCP}]^{0.97\pm0.25}[H_2O_2]^{1.38\pm0.30} \tag{6}$$

The rate is in mol/L·s, all concentrations are in mol/L, temperature is in K, and the activation energy is in J/mol. The uncertainties expressed in Eq. (6) are the 95% confidence intervals.

Fig. 6 shows the parity plot between the experimental 2,4-DCP conversions and those calculated from Eq. (4) with the optimized rate law parameters. This plot verifies that the estimated parameters provide a reasonable description of the experimental data. The rate constants are shown in Fig. 7 as temperature is varied. As expected, the reaction rate increased with an increase in the temperature.

3. Reaction Products from 2,4-DCP in SCWO

To understand the reaction mechanism of 2,4-DCP in SCWO, the intermediates were analyzed by using GC/MS. A sample at 0.074 mol/L H_2O_2, 400 °C and 230 bar condition was collected, and it was found that the aqueous products included a number of reaction intermediates, as shown in Fig. 8. These condensation products were identified with compounds in the GC/MS library that had higher than 90% reliability.

Juan et al. [2001] proved that hydrogen peroxide is a powerful source of highly reactive hydroxyl radicals ($H_2O_2 \rightarrow 2HO^\bullet$), and those radicals react rapidly and randomly with all organics present in the reaction medium. They showed that, due to the extremely high reactivity of radicals $HO^\bullet$, the generation of hydroxyl radical as a promo-

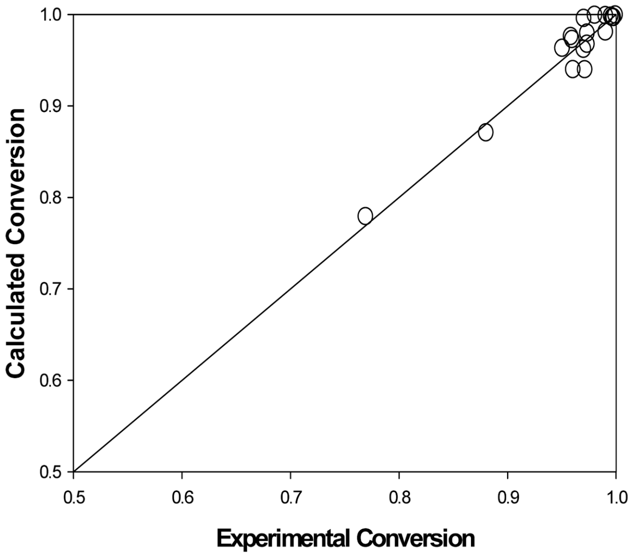

Fig. 6. Comparison of experimental and calculated 2,4-DCP conversions.

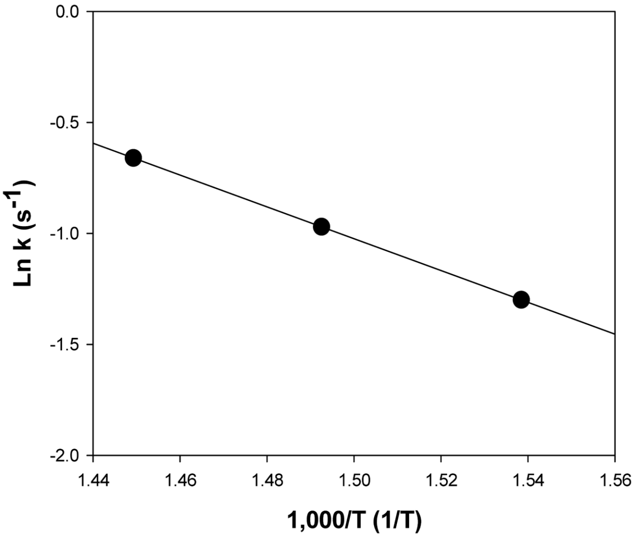

Fig. 7. Reaction rate constant at various temperature.

tion agent, HO$^\bullet$, can play a key role in the decomposition of organic compounds in the SCWO process [Savage et al., 1998; Motonobu et al., 1999]. Furthermore, the R$^\bullet$ formation reaction provides a powerful way to promote the oxidation of organics by generating the radicals R$^\bullet$ ($RH+HO^\bullet \rightarrow R^\bullet+H_2O$); and a Radical R$^\bullet$ can react with another R$^\bullet$ to form dimers ($R^\bullet+R^\bullet \rightarrow R-R$) [Juan et al., 2001].

Fig. 8 shows that the reaction products in this study consist of dichlorophenoxyphenol as a dimer, comparative high molecules (chlorohydroxybenzaldehyde and 3,5-Dichloro-2-hydroxyacetophene) and comparative low molecules (2-Methyl-2-chclopentene, phenol, 2-Methylphenol, 2,3-Dimethyl-2-Cyclopentene, 2,3,4-Trimethyl-2-Cyclopentene, 2-Methyl-5-Chlorophenol and 2,4-Dichloro-6-Methylphenol).

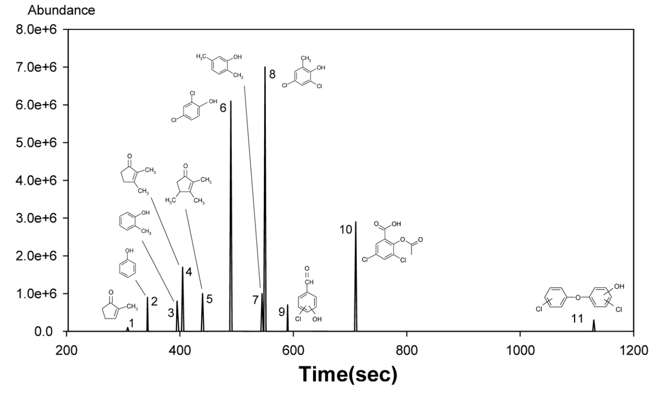

Fig. 8. Total ion chromatogram of 2,4-Dichlorophenol oxidation products at 230 bar, 400 °C, 6.135×10^{-3} mol/L 2,4-DCP and 0.147 mol/L H_2O_2.

1. 2-Cyclopentene, 2-Methyl
2. Phenol
3. Phenol, 2-Methyl
4. 2-Cyclopentene, 2,3-dimethyl
5. 2-Cyclopentene, 2,3,4-Trimethyl
6. Phenol, 2,4-Dichloro
7. Phenol, 5-Chloro, 2-Methyl
8. Phenol, 2,4-Dichloro, 6-Methyl
9. Chlorohydroxybenzaldehyde
10. 3,5-Dichloro-2-hydroxyacetophene
11. Dichlorophenoxyphenol

Consequently, it can be said that the reaction in SCWO using hydrogen peroxide is a free-radical reaction mechanism with radical formation, hydrogen abstraction, and radical shift reactions. The products identified as 3,5-Dichloro-2-hydroxyacetophene and Dichlorophenoxyphenol are the likely primary intermediates from the SCWO of 2,4-DCP. If so, the second pathway might lead to single-ring and ring-opening products such as phenol and carbon dioxide. The dimer could undergo secondary oxidation reactions to form ring-opening products and single-ring compounds in the SCWO process, and these products would be ultimately oxidized to CO_2.

CONCLUSIONS

2,4-Dichlorophenol was effectively oxidized by supercritical water with hydrogen peroxide in a batch reactor made of Hastelloy C-276. The effect of the oxidant amount on decomposition rate and efficiency was significant at near critical temperature, 380 °C. However, the effect of the oxidant concentration decreased with an increase in temperature, which is same as with the previous study [Lee et al., 2004]. Therefore, the reaction temperature in the SCWO process plays a key role in increasing the decomposition rate and efficiency of 2,4-DCP. The improvement of the decomposition reaction was not directly proportional to any increase in temperature from the critical temperature. The reaction kinetics for the decomposition of 2,4-DCP using SCWO was studied and the global reaction rate of 2,4-DCP oxidation in supercritical water was described.

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