OXIDATION CHARACTERISTICS OF PHTHALIC AND ADIPIC ACIDS BY SUPERCRITICAL WATER

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Abstract – Supercritical water oxidation (SCWO) was carried out in a flow-type reactor for modeling of wastewater containing phthalic or adipic acid. For each acid, the reaction order and rate constant, k, were determined over a wide range of experimental conditions: temperatures from 633.15 to 713.15 K, pressures from 18 to 29 MPa, excess amounts of hydrogen peroxide from zero to 800 percent, and the mean residence time in the reactor from 1.1 to 49.1 seconds. The concentration of both acids in model wastewater was set by 500 ppm. For phthalic acid, we found that the orders of decomposition reaction with respect to the reactant concentrations were 0.56 for phthalic acid, 0.31 for hydrogen peroxide, and 0.53 for water. For adipic acid, the orders of oxidation were 0.78 for adipic acid, 0.53 for hydrogen peroxide, and 0.74 for water. Then measured activation energy for phthalic acid was 33.08 kcal/mol and that for adipic acid was 19.51 kcal/mol, respectively.

Key words : SCWO, Decomposition, Phthalic Acid, Adipic Acid, Flow-type Reactor, Reaction Order, Reaction Constant, Activation Energy

INTRODUCTION

It is known that when a state of water is adjusted to a state above its critical condition (647.15 K and 22.12 MPa), it reaches a supercritical state. When a state of water stays in an ambient supercritical state, it behaves as a reactive solvent pertinent to decomposing various organic matters in wastewater streams. In recent decades, active research and process development work have been done to utilize the unique reactive properties of supercritical water (SCW) for the complete decomposition of various toxic and tenacious organic substances in wastewater [Pray et al., 1952; Shaw et al., 1991; Townsend et al., 1988]. Especially by virtue of recent active research on SCW oxidation (SCWO), this technology is emerging as a new environmentally benign process and ultimate solution for treating high toxic chemical, biochemical, and pharmaceutical wastes in water streams [Caruana, 1995].

Due to its highly reactive properties, SCW shows high affinity with various nonpolar water pollutants such as polychlorinated biphenyl and similar substances. Also, SCW can be used as a reaction medium of various substances in water such as oxygen, nitrogen and helium since they show high solubility in SCW [Carauna, 1995]. The SCWO process is similar to wet air oxidation (WAO) and incineration in a certain aspect. However, the SCWO of organic substances can proceed in closed-loop equipment with moderately low temperature without discharging flue streams when compared to WAO and incineration. As a result, one can be free from the generation of air pollutants such as NO_x and SO_x in the SCWO processes.

Various works on SCWO are in progress worldwide, with emphasis on the understanding of the oxidation reaction mechanism and the characteristics of decomposed gaseous compounds for aqueous phenol [Thornton and Savage, 1990, 1992; Li et al., 1992], for acetic acid [Meyer et al., 1995], for p-chlorophenol [Yang and Eckert, 1988] and many others. Also efforts have been made on the effect of catalyst on SCWO of 1,4-dichlorobenzene [Jin et al., 1992] and the quantitative analysis of decomposed gaseous compounds [Killilea et al., 1992]. In recent years, nationally and internationally, Korean investigators have also been deeply involved in the SCWO of waste pollutants [Lee and Gloyna, 1990, 1992; Lee et al., 1997; Joung et al., 1997].

Recently the present authors carried out experimental evaluation of SCWO for decomposition of phenol in model wastewater [Joung et al., 1997]. As an extension of the previous work, phthalic and adipic acids were selected and SCWO of these was performed to evaluate the oxidation rates and reaction orders. In domestic industries, a large amount of wastewater which contains such water pollutants as phenol, phthalic acid and adipic acid is generated in the production of hydrogen peroxide. In the present study, we report experimental information on SCWO of phthalic and adipic acid for providing engineering guidelines for the design and construction of SCWO processes.

SCWO KINETICS

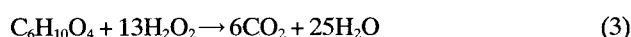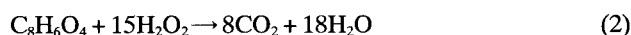One of essential parts in experimental SCWO studies of

organic substances is the quantitative determination of the reaction constant, k, and the order of reaction. In this regard, we assumed the reaction proceeds in a plug flow reactor since we used a tubular type of SCWO reactor (o.d., 3.17 mm). Under this assumption the design equation for a tubular reactor [Thornton and Savage, 1990; Meyer et al., 1995] is given by

$$\frac{\tau}{C_o} = \int_o^X \frac{dX}{-R} \qquad (1)$$

Where τ denotes residence time in seconds, X the conversion of reactants, C_0 the initial concentration of reactants, and R the reaction rate expression.

Under the assumption that phthalic acid and adipic acid are oxidized completely by SCW, the stoichiometric expression for each acid is written by

$$C_8H_6O_4 + 15H_2O_2 \rightarrow 8CO_2 + 18H_2O \qquad (2)$$

$$C_6H_{10}O_4 + 13H_2O_2 \rightarrow 6CO_2 + 25H_2O \qquad (3)$$

Based on Eqs. (2) and (3), the reaction rate expression is written in terms of the reaction rate constant, k and the order of reaction a, b, c for each acid.

$$R = k[Organic]^a [H_2O_2]^b [H_2O]^c \qquad (4)$$

Since the molar volume of reactants can be assumed as constant at a fixed temperature in a tubular reactor, the effect of residence time on the reaction conversion can be written in terms of initial concentration of reactants and the percent conversion. Thus, by combining Eqs. (1) and (3), it is written by

$$\frac{dX}{d\tau} = k[Organic]_o^{a-1}(1-X)^a [H_2O_2]^b [H_2O]^c \qquad (5)$$

During reaction the concentration of water can be assumed to stay as a constant since the content of water is more than 99 % in SCWO. Therefore, $[H_2O]^c \approx [H_2O]_0^c$ in Eq. (5). Also, one may assume $[H_2O_2]^b \approx [H_2O_2]_o^b$ within a reasonably acceptable error range of about 20 % since an excess amount of hydrogen peroxide (>300 %) is frequently supplied to the reactor in SCWO [Thornton and Savage, 1992]. Thus Eq. (5) can be rewritten as an analytical form of linear differential equation.

$$f(X) = \int_o^X \frac{dX}{(1-X)^a} = k \tau [Organic]_o^{a-1}[H_2O^2]_o^b[H_2O]_o^c \qquad (6)$$

This expression can be used as a fundamental equation for the evaluation of SCWO reaction kinetics [Thornton and Savage, 1992]. By Eqs. (5) and (6), the constants a, b, and c and k can be determined from experimental information. In determining k, we assumed $k=k_o exp(-E_a/RT)$ and drew an Arrhenius plot in terms of lnk and 1/T. From this plot, k_o and the activation energy E_a are determined.

EXPERIMENTAL

1. Reagents

Phthalic acid (99 %) and adipic acid (99 %) were purchased from Aldrich Chemical Co., USA. For both acids, model

Table 1. Pure physical properties of phthalic acid and adipic acid

Name	Formula	Molecular weight	T_m [K]	T_b [K]
o-Phthalic acid	$C_8H_6O_4$	166.13	483.15	-
Adipic acid	$C_6H_{10}O_4$	146.14	426.15	538.15

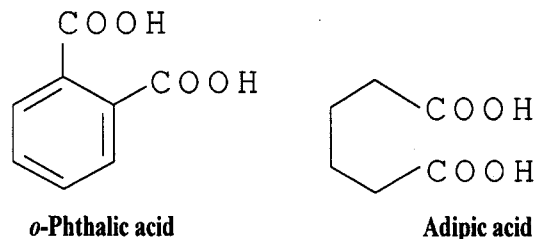

o-Phthalic acid   Adipic acid

Fig. 1. Chemical structures of phthalic and adipic acid.

wastewater containing 500 ppm of each acid was prepared. Distilled water is used to make SCW. Also 28-mol % of hydrogen peroxide is used as an oxidant. The basic physical properties and chemical formula are given in Table 1 and Fig. 1, respectively. The excess amount of hydrogen peroxide in accordance with the different stoichiometric ratios is calculated by Eqs. (2) and (3).

2. Experimental Apparatus

The schematic diagram of the experimental SCWO equipment is shown in Fig. 2. The major parts consist of a pressurization device, heating, preheating and their temperature controllers, cooling device and pressure control device. All parts such as tubes, fittings, and valves are stainless steel 316 products from HIP Co., USA. From the preliminary test, we found that the equipment could be safely used up to 723.15 K.

A high-pressure double-head pump was purchased from Milton Roy Co., USA. This pump can pressurize a liquid feed up to 45.0 MPa. One head of the pump was used to pump the model wastewater and the other was used for pumping hydrogen peroxide solution. A backpressure regulator (TESCOM, USA) controls the pressure in the equipment. Heating tapes were used to heat the transporting lines and preheaters. All heating parts such as preheaters were insulated by Gypsum
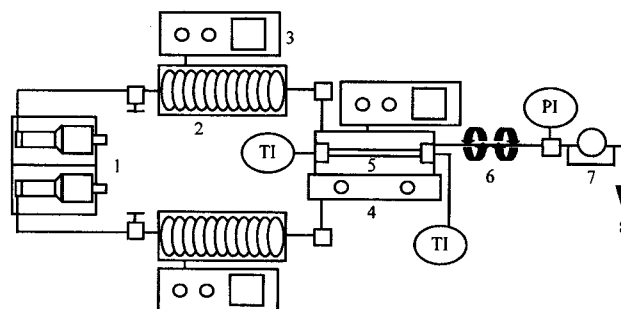

Fig. 2. Schematic diagram of supercritical water oxidation apparatus.

1: Liquid pump	5: Tubular reactor
2: Preheater	6: Thermal exchanger
3: Temperature controller	7: Backpressure regulator
4: Furnace	8: Sampling

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tape and a furnace (Kwangmyung Electric Co., Seoul, Korea) heated the main SCWO reactor. The system temperature was regulated by a PID controller (HY-P100, Hanyoung Co., Seoul, Korea), and the pressure was measured by a barometer from VALCOM Co., USA.

The SCWO reactor (o.d. is 3.17 mm and internal volume is 6.4 cm³) was built to operate in a continuous manner. The effluent reaction products from the reactor were cooled by passing through a flow cooler (FC-500, Techne, Seoul, Korea) to prevent further oxidation outside the reactor.

3. Procedure

Experimental variables for the SCWO of phthalic and adipic acids are temperature (633.15, 653.15, 673.15, and 713.15 K), pressure (18, 20, 23, 26, and 29 MPa), initial concentration of acid in model wastewater, flow rate of feed solutions (e.g., mean residence time) and percent of excess hydrogen peroxide, respectively.

To obtain necessary experimental data for the determination of the reaction constants and orders, experiments were performed in the following sequence: first, the model wastewater and hydrogen peroxide solution were fed separately to the system via preheaters with constant flow rates. Then, the pressure inside the reactor system was adjusted and controlled by the backpressure regulator. The excess amounts of hydrogen peroxide were set by 0, 300, 600, and 800 %. The percent excess was calculated from the 28-mol % hydrogen peroxide solution fed to the system.

The pressure was controlled within 0.2 MPa and the temperature inside the reactor was maintained within 1.0 K. The effluent products from the reactor were analyzed as described in the next section.

4. Analytical Methods

The degree of oxidation of phthalic acid was analyzed by a UV/VIS Spectrophotometer (V-550, Jasco Co., Japan). After the light absorbance was checked in the range of wavelength from 190 to 800 nm, an analysis was made at a wavelength of 280 nm. The calibration curve for the concentration of unreacted phthalic acid against the absorbance was constructed, and from this the conversion was determined. For adipic

Table 2. UV/VIS spectrophotometer conditions for analysis of phthalic acid concentration

Apparatus	Jasco Spectrophotometer V-560
Fixed UV wave length [nm]	280
Standard Solution	HPLC Water
UV Cell Volume	3.5 ml

Table 3. Gas chromatograph conditions for analysis of adipic acid concentration

Column	HP ultra 1 (cross-linked methylsiloxane)
	25 m L.×0.32 mm I.D.×0.25 nm film thick.
Detector	FID
Helium flow rate	3.85 ml/min
Split ratio	20:1
Injector temperature	473.15 K
Detector temperature	553.15 K
Column temperature	423.15 → 553.15 K (8 K /min)

acid, however, the degree of reaction was determined by a gas chromatograph (HP 5890 series II, USA) with an FID detector. Helium was used as a carrier gas. Analysis conditions for phthalic acid and for adipic acid are summarized in Tables 2 and 3.

RESULTS AND DISCUSSION

Fig. 3 shows typical results for the conversion of phthalic acid by SCWO at 673.15 K and 26 MPa, which is plotted against the residence time with different excess amounts of hydrogen peroxide. Under the same reaction conditions, SCWO results for adipic acid are shown in Fig. 4. Experimental data
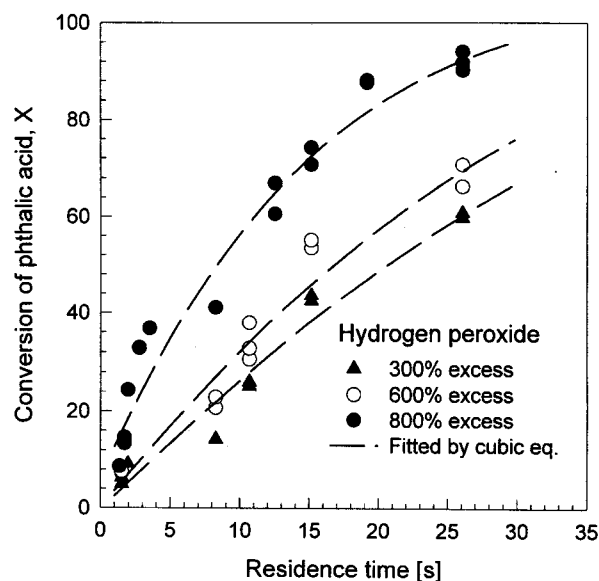

Fig. 3. Conversion of phthalic acid against residence time with different excess hydrogen peroxide (673.15 K, 26 MPa, and 500 ppm phthalic acid).
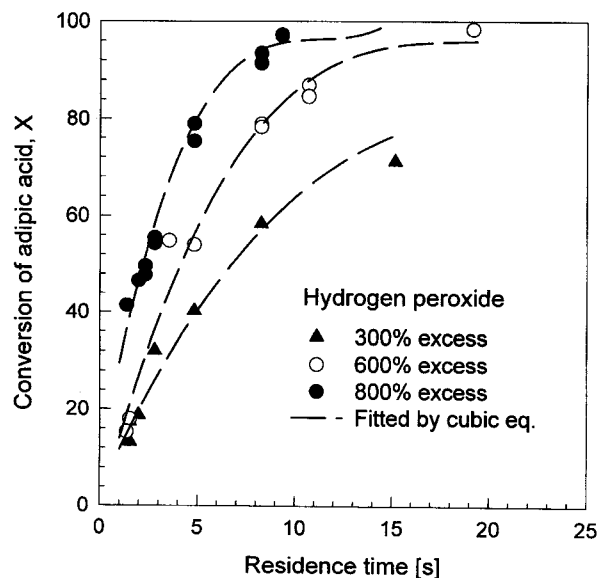

Fig. 4. Conversion of adipic acid against residence time with different excess hydrogen peroxide (673.15 K, 26 MPa, and 500 ppm adipic acid).
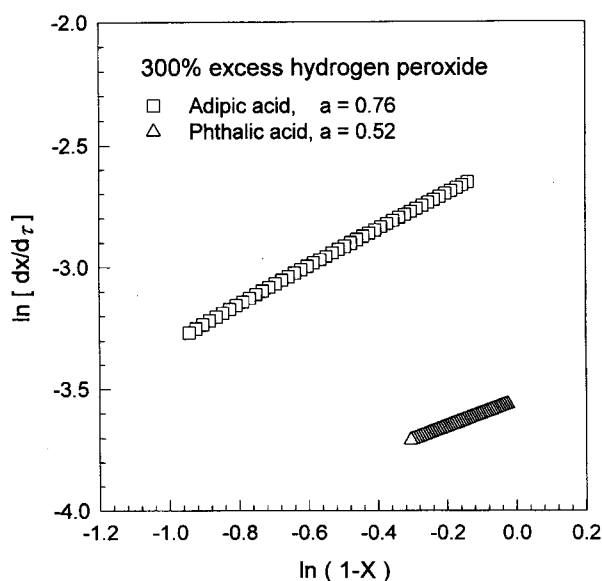
Fig. 5. Measured and calculated orders of reaction with respect to phthalic acid and adipic acid concentration.

Fig. 6. Measured and calculated orders of reaction with respect to H_2O_2 concentration.

relation.

$$k[H_2O]_o^c = \frac{[(1-X)_o^{1-a} - 1]/(1-a)}{\tau[Organic]_o^{a-1} [H_2O_2]_o^b} = G(X) \qquad (8)$$

In determining c, additional experiments were carried out at 500 ppm acid concentration, 673.15 K and 800 % excess amount of hydrogen peroxide by varying pressures from subcritical to supercritical condition of water (18, 20, 23, 26, and 29 MPa). Also, the concentrations of SCW (l.h.s. of Eq. (8)) were obtained from the information on the variation of water density at different pressures based on data available in literature [Harr et al., 1984]. Then, c was determined based on Eq. (8) in terms of $\ln[G(X)]$ and $\ln[H_2O]_o$ as shown in Fig. 7. The best-fitted values of c were 0.53 for phthalic acid and 0.74 for

for both acids are also correlated by a cubic expression of conversion as a function of residence time at a fixed excess amount of hydrogen peroxide, $X = f(\tau)$.

The conversion increased significantly with increasing excess amount of hydrogen peroxide. To determine a, the order of reaction, a differential method was used. To do this, each conversion curve represented by the cubic curve fitting as shown in Figs. 3 and 4 was used to fit again the data in terms of $\ln(dX/d\tau)$ and $\ln(1-X)$ as shown in Fig. 5. Although only the calculated results for 300 % are shown in Fig. 5, similar calculations were carried out at 600 and 800 % of excess amount of hydrogen peroxide. For phthalic acid, the reaction order a with respect to the excess amount of hydrogen peroxide was 0.52, 0.60, and 0.56, respectively. Thus, we determined a as 0.56 by averaging the measured values. Also, for adipic acid, the a with respect to the excess amount of hydrogen peroxide was 0.76, 0.78 and 0.80, respectively, and we chose a as 0.78 by averaging the measured values.

Based on the best-fitted mean values of a for phthalic acid and for adipic acid, the other order of reaction, b, was determined from Eq. (6). In doing so, Eq. (6) was rearranged to

$$f(X) = \frac{1}{1-a} [(1-X)^{1-a} - 1] = k \tau[Organic]_o^{a-1}[H_2O_2]_o^b[H_2O]_o^c \quad (7)$$

As discussed previously in relation to Figs. 3 and 4, the order of reaction, a stays as a constant at a given excess amount of hydrogen peroxide. Based on these observations, b was calculated. To do this, the data were plotted in terms of $\ln[\{(1-X)^{1-a}-1\}/\{\tau(1-a)\}]$ and $\ln[H_2O_2]_o$ and from these b's were determined as demonstrated in Fig. 6. As shown in Fig. 6, the best-fitted value of b for phthalic acid was 0.31 and that for adipic acid was 0.53. The order of reaction with respect to the concentration of water, c, was determined by utilizing the values of a and b by fitting the data using the following
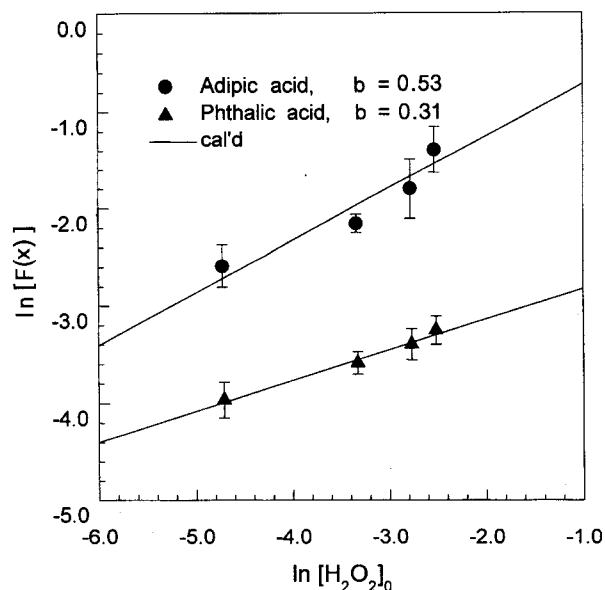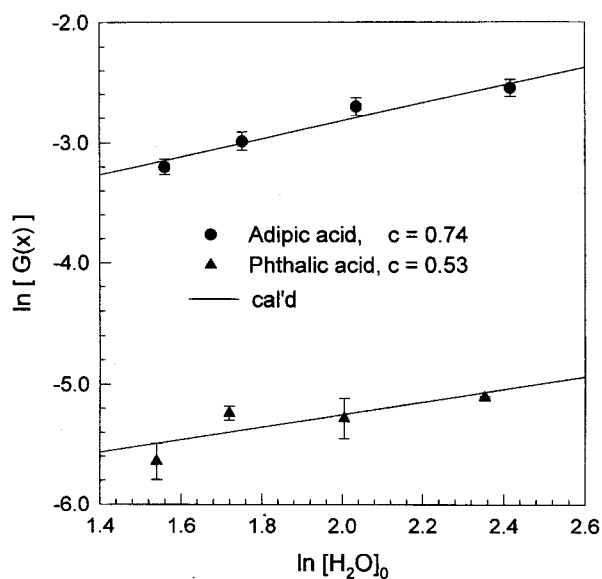

Fig. 7. Measured and calculated orders of reaction with respect to H_2O concentration.

adipic acid.

The other essential information on the SCWO of the acids is the reaction constant, k. This was obtained by fitting experimental data obtained with varying temperatures (i.e., 633.15, 653.15, 673.15, and 713.15 K) at an isobaric condition, 26 MPa. In these experiments, the initial concentration of each acid was 500 ppm and the excess amount of hydrogen peroxide was fixed at 800 %. With these different conditions, the conversions with respect to the residence time were taken. To estimate k_o and E_a as a function of temperature, $\ln[k]$ was plotted against $1/T$ as shown in Fig. 8. For phthalic acid, the estimated values of k_o was 5.35×10^7 $M^{-0.39}$/s and the activation energy, E_a was 33.08 kcal/mol. For adipic acid, k_o was 4.7×10^4 $M^{-1.07}$/s and E_a was 19.51 kcal/mol.
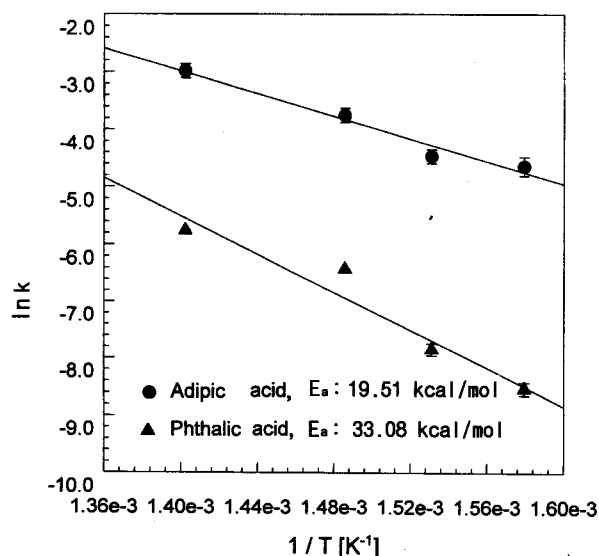
Finally, to compare grossly the experimental and calculat-

Fig. 10. Comparison between measured and calculated conversions of adipic acid.

Table 4. Values of reaction-order and Arrhenius parameter

	Phthalic acid	Adipic acid
a	0.56	0.78
b	0.31	0.53
c	0.53	0.74
E_a (Kcal/mol)	33.08	19.51

ed results, measured and calculated conversions were plotted in Fig. 9 for phthalic acid and in Fig. 10 for adipic acid, respectively. In general the calculated and experimental data agree well and, thus, the values of a, b, c, and k obtained in the present study can be used for the purpose of SCWO processes for a wastewater containing the two acidic substances.

Fig. 8. Arrhenius plot of oxidation of phthalic and adipic acid in supercritical water.

CONCLUSION

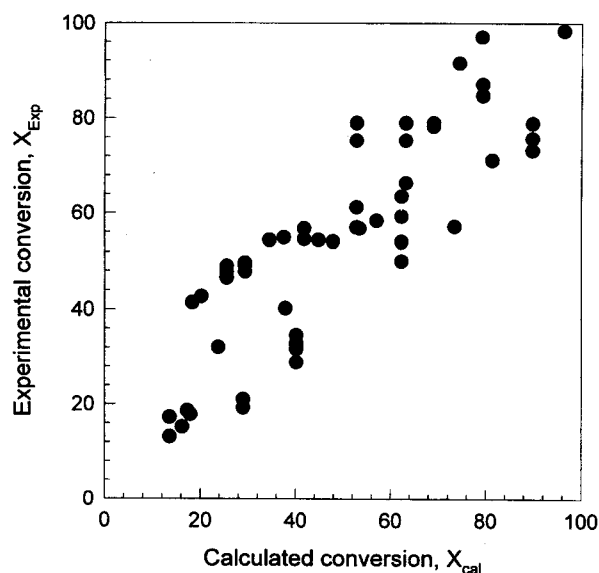To understand the decomposition characteristics of phthalic and adipic acids by SCWO, we performed experiments at various conditions. These results are summarized in Table 4. Although the model wastewater used in the present work is not the real one, this information can be used as an engineering guide for treating real wastewater containing phthalic or adipic acid. We found that through the SCWO more than 99 % decomposition can be easily accomplished for both acids.

ACKNOWLEDGMENT

NOMENCLATURE

Fig. 9. Comparison between measured and calculated conversions of phthalic acid.

a   : reaction order for o-phthalic acid or adipic acid
b   : reaction order for hydrogen peroxide
c   : reaction order for water

C_o : initial concentration of o-phthalic acid or adipic acid [mol/L]

E_a : activation energy [kcal/mol]

k : global reaction rate constant

k_o : Arrhenius pre-exponential factor

P : system pressure [MPa]

P_c : critical pressure [MPa]

R : rate of reaction

T : system temperature [K]

T_b : normal boiling temperature [K]

T_c : critical temperature [K]

T_m : melting temperature [K]

X : conversion of o-phthalic acid or adipic acid

Greek Letter

τ : reactor residence time [s]

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