



ELSEVIER

Journal of Hazardous Materials B73 (2000) 245–254

**Journal of
Hazardous
Materials**

www.elsevier.nl/locate/jhazmat

Supercritical water oxidation of high concentrations of phenol

Yukihiko Matsumura^{a,*}, Teppei Nunoura^b, Taro Urase^a,
Kazuo Yamamoto^a

^a Environmental Science Center, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 Japan

^b Urban Engineering Department, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 Japan

Received 20 August 1999; received in revised form 20 November 1999; accepted 21 November 1999

Abstract

Decomposition of phenol at a concentration as high as 2 wt.% was effected by supercritical water oxidation at 25 MPa. Reaction temperatures ranged from 623–723 K and residence times were varied from 6.5 to 26 s. Oxygen was added in an equivalent amount to investigate reaction intermediates. The degree of phenol decomposition and reaction product were measured. Although tarry material production was observed, phenol decomposition conversion was predicted well by the reaction rate equations developed by previous researchers who conducted experiments at lower concentrations. Difference from low concentration phenol oxidation was found in the reaction product distribution and tarry material production. One possible explanation for this result is that the initiation of phenol decomposition is the same regardless of phenol concentration but that the succeeding radical reactions are different. The additive reaction between aromatic compounds was enhanced by high phenol concentration. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical water; Phenol; Oxidation; High concentration; Tar

Abbreviations: *a*, Reaction order for phenol (–); *b*, Reaction order for oxygen (–); *C*, Concentration (M); *c*, Reaction order for water (–); E_a , Activation energy ($J \cdot mol^{-1}$); k_0 , Pre-exponential factor [$M^{1-a-b-c} \cdot s^{-1}$]; *R*, Gas constant ($J \cdot mol^{-1} \cdot K^{-1}$); *T*, Temperature (K); *t*, Time (s); ϕ , Decomposition conversion (–); *f*, Final; H₂O, Water; *i*, Initial; O₂, Oxygen; *ph*, Phenol

* Corresponding author. Tel.: +81-3-5841-2974; fax: +81-3-5802-8887.

E-mail address: matumura@esc.u-tokyo.ac.jp (Y. Matsumura).

1. Introduction

Supercritical water oxidation (SCWO) is a promising technology for treatment of wastewater containing hazardous organic compounds. The high efficiency with which SCWO decomposes stable organic compounds with an aromatic structure has attracted many researchers as well as commercial process vendors. Sako et al. [1] found that perchlorinated dibenzo-*p*-dioxines and perchlorinated dibenzofurans in fly ash can be decomposed to less than 1% using SCWO at 673 K. It is known that at temperatures as high as 873–903 K, 2,3,7,8-dibenzo-*p*-dioxines, tetra- and octa-chlorinated dibenzofuran, and octachlorinated dibenzo-*p*-dioxin are decomposed with a destruction efficiency higher than 99.9% at a residence time as short as 5 s [2]. SCWO is an approved treatment technology to decompose polychlorinated biphenyl in Japan.

However, the high operational cost of the SCWO process prevents its wide use. The reason for this high cost results partly from the high capital cost of the reactor that is operated at pressures higher than 22.1 MPa and temperatures higher than 647 K, and partly due to the cost of electricity needed to run the air compressor. A lower reaction temperature and a smaller amount of air are thus wanted, but operation at lower temperatures with less oxygen will lead to incomplete decomposition and tarry material production. Hence, it is critical to determine to what extent the operational temperature can be lowered and oxygen supply can be reduced while maintaining the high destruction efficiency.

Another desirable condition for SCWO is a high concentration of organic feed. Heating the feed stream to supercritical temperatures requires large amount of heat. If one wants to provide this heat from the heat of combustion of organic feed, a feed concentration around 5 wt.% is needed. Otherwise, the additional process heat must be supplied. When this is the case, organic fuel is often added to the feed stream.

A high concentration of organic feed causes another problem. Xu et al. [3] pointed out that organic compounds at high concentration produce tarry material in supercritical water when no catalyst is added (see also Yu et al. [4]). Although their gasification operation was conducted in the absence of oxygen, the same reaction is expected when oxygen supply is decreased to reduce operational cost. Rice et al. [5] reported that organic compounds at higher concentrations decrease conversion in supercritical water oxidation. Formation of a heavy compound such as char reduces process effectiveness because of the difficulty in decomposing the compound formed. The possible plugging of the reactor by the compound formed is another problem. A higher concentration of organic feed also increases demand of oxygen for complete decomposition of the feed.

It is critical for the economical operation of SCWO that one determine least amount of oxidant and lowest temperature at which complete decomposition of organic compounds is still achieved and no tarry material is formed. For this purpose, understanding of the reaction mechanisms of SCWO at a high organic feed concentration is essential. However, to date SCWO of high concentration feed with low oxygen supply has not been investigated.

The SCWO reaction mechanism for low concentration feeds has been studied by many researchers. One of the most published researchers is Prof. Savage of University of Michigan. Savage and his co-workers have studied supercritical oxidation of phenol

beginning with the determination of global reaction rates [6,7], followed by the identification of reaction intermediates [8] and reaction pathways [9], decomposition characteristics of substituted phenol [10], and radical reaction network derivation [11,12]. Recently, Savage et al. employed CHEMKIN, a radical reaction simulator and database, to understand and describe methanol oxidation in supercritical water [13]. Other mechanism-based models for SCWO were employed by Holgate and Tester [14]. They developed a model for oxidation of simple molecular compounds such as hydrogen and carbon monoxide. Crain et al. [15] developed a network model of pyridine oxidation in supercritical water. These investigations are basically conducted for feed concentrations lower than 0.1 wt.% to achieve a controllable reaction temperature without disturbance by the heat of reaction. Although this low concentration enables detail kinetic study, additive reactions to produce tarry material are not considered because of the low reactant concentration.

To understand the reaction mechanism for a practical operating condition, the decomposition of organic compounds at a high concentration is significant. The effect of additive reactions, which result in a tar-like material, cannot be determined in low-concentration experiments. The effectiveness of the reaction rate equation obtained at low concentrations must also be examined. Thus, the purpose of this study was to conduct supercritical water oxidation of phenol at a high concentration in order to investigate the effect of additive reactions, and to examine the validity of the rate equations obtained by experiments at low concentration.

2. Experiments

Fig. 1 shows the experimental apparatus employed in this study. The apparatus consisted of two HPLC pumps to feed organic material and hydrogen peroxide, a reactor in which both streams are mixed and oxidation takes place, an effluent collecting section

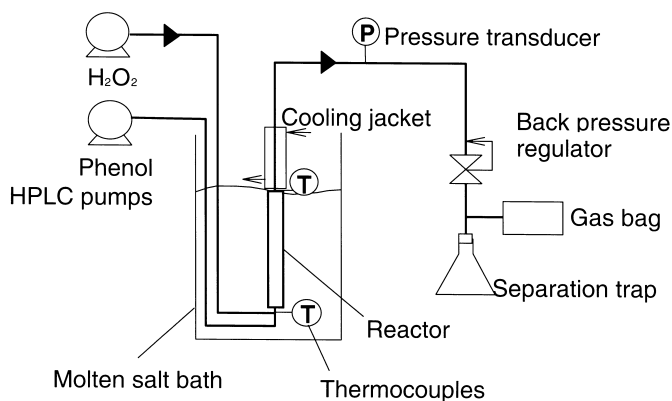


Fig. 1. Experimental apparatus.

where gas and liquid are collected separately, and a molten salt bath to maintain the reactor temperature. As a model compound, phenol was tested in this reactor system because it is known to be a difficult compound to decompose compared to other substituted phenols [10], and its rather high solubility in water allows a constant feed. Several investigations of supercritical water oxidation of phenol have been carried out, and reference data for low concentration experiments are available [6,7,16,17].

An aqueous solutions of phenol and hydrogen peroxide were pressurized by separate HPLC pumps and heated to the reaction temperature in the preheating section located in the molten salt bath. Hydrogen peroxide decomposed completely into water and oxygen by the time when it was mixed with phenol. This phenomenon was examined by changing the length of the pre-heating section, and also is supported by the hydrogen peroxide decomposition rate measured by Croiset et al. [18]. The two streams were mixed in the tee located just before the reactor, and then fed into the reactor. Stainless steel tubing (2.17 mm i.d. \times 3.17 mm o.d.) was employed as a reactor. Changing the length of the tubing allowed experiments at different residence times. At the exit of the molten salt bath, the effluent was rapidly cooled using a heat exchanger to terminate the reaction. Effluent was then depressurized by a back pressure regulator, and delivered to a separation trap, where the gas was separated from liquid phase and collected in a gas bag. Prior to feeding reactants, only water was fed to the reactor until the desired temperature and pressure were achieved. Then, the reactants were pumped into the system. It was only after the steady state was achieved that the effluent was sampled.

Gaseous products were analyzed using a GC-TCD (Shimadzu GC/8A). The gas sample was a mixture of effluent gas and air in the gas–liquid separator. Employing a dilution factor for nitrogen and the known volume inside the gas–liquid separator allowed calculation of the amount of product gas. For a residence time of 26 s, the value of dilution factor was approximately 7 at 673 K, 25 MPa. The concentration of phenol in the liquid phase was measured by HPLC. Prior to the analysis, the effluent was filtered using a membrane filter (DISMIC-13P, Cellulose acetate, effective pore size 0.45 μm). Intermediate compounds from oxidation reactions were extracted by dichloromethane and analyzed by GC-MS (HP-6890, HP-5973).

The decomposition conversion of phenol was determined by the following equation:

$$\phi = \frac{C_i - 2C_f}{C_i} \quad (1)$$

where C_i and C_f are the phenol concentrations of feed and effluent samples, respectively. Note that the phenol solution is diluted by a factor of two because of being mixed with an equal amount of hydrogen peroxide aqueous solution.

The phenol concentration employed in this research was as high as 2 wt.%. This concentration is higher than utilized in previous experiments by a factor of 10 to 100, and allows examination of the effect of additive reactions. These conditions also allow the examination of the validity of rate equations obtained in previous experiments at low phenol concentrations. The concentration of hydrogen peroxide utilized was such that an equivalent amount of oxygen to phenol feed was achieved. Since 1 mol of phenol consumes 7 mol of oxygen, the molar concentration of hydrogen peroxide was 14 times

higher than the phenol molar concentration. Previous researchers preferred to run experiments at a much higher oxygen/phenol ratio, to show that complete conversion is possible, but the concentration was set low in order to determine the effect of low oxygen concentration, which will reduce operating cost. Production of tarry material and intermediate products could be expected at this condition. The feed rates of both phenol and hydrogen peroxide solution were set at $1 \text{ g} \cdot \text{min}^{-1}$. The reaction temperature was varied from 623 to 723 K, measured both at the entrance and exit of the reactor, and controlled with a temperature controller. The reaction pressure was set at 25 MPa and measured just before the back pressure regulator.

To maintain a single phase inside the reactor, a pressure higher than critical pressure is necessary, but higher operating pressures result in higher power requirements for oxygen compression. This pressure also causes problems regarding the reactor wall stress.

3. Results and discussion

3.1. Effect of heating section

A series of preparatory experiments was conducted to determine the effect of heating section length so that condition to achieve complete decomposition of hydrogen peroxide can be found. The hydroxyl radical found in the early stage in the hydrogen peroxide decomposition is known to be more reactive than oxygen itself. Thus, insufficient decomposition of hydrogen peroxide will result in higher decomposition of phenol. The experiments were carried out at 673 K, 25 MPa. A hydrogen peroxide concentration of 10% was employed; this concentration is much higher than that employed for the oxidation of phenol. Table 1 shows the result of this experiment. Changing the length of preheating section by 2, 4, and 8 m did not affect the phenol decomposition conversion, and the 2-m length for preheating section was found to be sufficient.

3.2. Effect of reaction temperature

Fig. 2 shows the effect of reaction temperature on the phenol conversion. By changing the length of the reactor corresponding to the density of water at each

Table 1
Effect of the heating length on hydrogen peroxide decomposition

Length of the heating zone (m)	Phenol decomposition conversion (–)
2	0.578
4	0.592
8	0.528

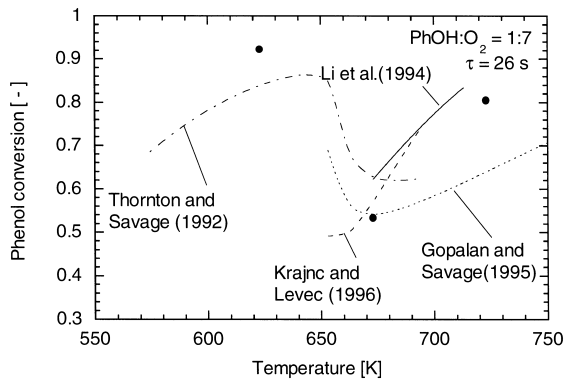


Fig. 2. Effect of reaction temperature on phenol conversion.

temperature, the residence time for all runs was maintained at 26 s. Fig. 2 also shows the decomposition conversion predicted by previous studies conducted at much lower concentrations of phenol. Previous researchers [6,7,16,17] determined the overall reaction conversion for phenol oxidation as:

$$\frac{dC_{\text{ph}}}{dt} = k_0 \exp\left(\frac{-E_a}{RT}\right) C_{\text{ph}}^a C_{\text{O}_2}^b C_{\text{H}_2\text{O}}^c \quad (2)$$

where k_0 , E_a , R , T , t and C expresses pre-exponential factor, activation energy, gas constant, absolute temperature, time, and molar concentration of each species, respectively. Subscripts ph, O_2 , and H_2O denotes phenol, oxygen, and water; and a , b , and c denotes exponent for each concentration, respectively. Coefficients used for the prediction are shown in Table 2. The prediction from previous studies yields a sigmoid curve with local maximum and minimum points, because the order of reaction with respect to water concentration has a positive value. An increase in the temperature has the effect of lowering water concentration due to a density decrease as well as increasing the reaction rate itself. The sigmoid shaped curve is the result of these two opposite effects.

Interestingly, despite the fact that our experiments employed phenol concentration almost two orders of magnitude higher than previous studies, prediction of conversion based on previous studies is in good agreement with our experimental results. This fact implies that decomposition of phenol can be expressed by a single reaction rate equation for a broad range of phenol concentration. Namely, the reaction rate equation obtained by experiments at concentrations as low as 100 mg L^{-1} is still valid for the reaction with concentration as high as 2 wt.%.

The effect of residence time on the yields of gas and dimer are shown in Fig. 3. The gas yield is less than 0.1. Although the phenol conversion increases with the increase in residence time, gas yield and dimer yield do not show sufficient increase to match the increase in the conversion; this result indicates an unclosed mass balance. On the contrary, experiments conducted at lower concentrations show almost a closed mass

Table 2
Global kinetic models for SCWO of phenol

Researchers	Reactor type	Kinetic parameters					No. of runs	Temperature (K)	Pressure (MPa)	$C_{\text{ph},i}$ (mM)
		k_0 ($\text{M}^{1-a-b-c} \text{s}^{-1}$)	E_a (kJ mol^{-1})	a (-)	b (-)	c (-)				
Li et al. (1994)	Pilot plant	1970	60.8	1	0	0	31	677–715	25	6.3–8.2
Thornton and Savage (1992)	Flow	303	51.8	1	0.5	0.7	159	573–693	19–28.2	0.2–5.8
Gopalan and Savage (1995)	Flow	219	51.8	0.85	0.5	0.42	148 ^a	653–693	25.3	29.9–388
Krajnc and Levec (1996)	Flow	4.90×10^8	124.8	1.04	0.38	0	63 ^a	653–723	23–26.5	5.6–11.1

^aCountable data points on parity plot.

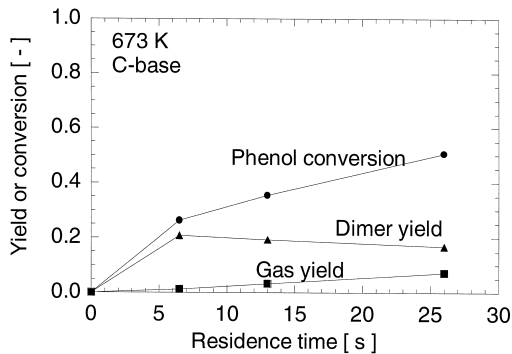


Fig. 3. Effect of residence time on product yields.

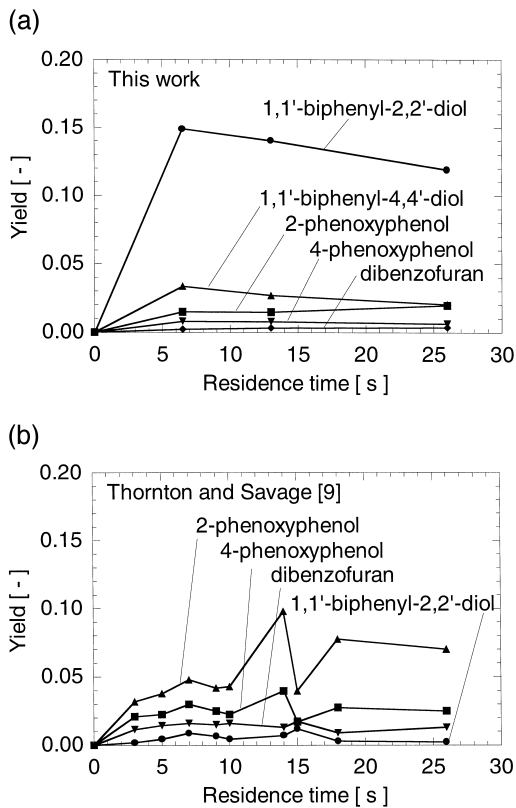


Fig. 4. (a) Yield change of dimer products with increasing residence time (This work). (b) Yield change of dimer products with increasing residence time [9].

balance [6]. After an experimental run, we found tarry material at the back pressure regulator, which is probably be the reason for this unclosed mass balance. This finding indicates that when one treats a high concentration phenol solution, production of tarry material should be considered. Quantitative recovery of this tarry material was not possible, and further conclusions cannot be made.

Fig. 4 shows the change of yield of some dimer products with residence time for oxidation of 2% phenol at 673 K, 25 MPa. The results from Thornton and Savage [9] are also shown; these data were obtained by oxidation of 100 mg L^{-1} with 800% excess oxygen at 653 K, and 28.2 MPa. The distribution of product dimer compounds is completely different from this earlier work. For our experiment conducted with 2 wt.% solution (Fig. 4a), much more 1,1'-biphenyl-2,2'-diol is produced than Thornton and Savage (Fig. 4b) found. It is also to be noted that the yields of these compounds are much higher in this experiment. This fact shows that additive reactions between aromatic compounds are favorable in the reaction field with high phenol concentration.

The increase in phenol concentration in the feed will increase radical product concentrations. However, if the order of reaction of the radical is unity, the product yield will not be affected. Thus, it is necessary to consider a reaction mechanism of a higher reaction order. Gopalan and Savage [19] have presented a thorough discussion of the reaction mechanism for phenol oxidation based on free radical chemistry. Applicability of their model to the higher concentrations employed in this study should be investigated in future work. It is to be noted, however, that tarry material produced in this study should be considered in the radical reaction mechanism for decomposition of phenol at a high concentration. For application of supercritical water oxidation to industrial waste, this approach should be of importance.

Considering the fact that Fig. 2 shows good agreement between our experimental results and prediction based on the data obtained at a low concentration, one possible mechanism is that radical formation by phenol decomposition is first-order as a function of phenol concentration. Existence of radical reactions of with a reaction order higher than unity explains the difference between the results obtained by Gopalan and Savage [19] and this work.

4. Conclusions

Supercritical water oxidation of phenol at a concentration as high as 2 wt.% was conducted with stoichiometric amount of oxygen at 25 MPa. Reaction temperatures ranged from 623 K to 723 K and residence times from 6.5 to 26 s. Phenol decomposition conversions as well as reaction products were measured. Phenol decomposition conversions were successfully predicted by the reaction rate developed by previous research conducted at concentrations as much as two orders of magnitude lower than this work. Differences from low concentration phenol oxidation were found in the reaction product distribution and tarry material production. One possible explanation for this result is that initiation of phenol decomposition is the same regardless of phenol concentration but that the succeeding radical reactions are affected by radical concentration. The additive reaction between aromatic compounds was favored by high phenol concentration.

Acknowledgements

Y.M. is grateful for the financial support from the Foundation for Earth Environment.

References

- [1] T. Sako, T. Sugeta, K. Otake, M. Sato, M. Tsugumi, T. Hiaki, M. Hongo, *J. Chem. Eng. Jpn.* 30 (1997) 744.
- [2] K.C. Swallow, W.R. Killilea, *Environ. Sci. Technol.* 26 (1992) 1849.
- [3] X. Xu, Y. Matsumura, J. Stenberg, M.J. Antal Jr., *Ind. Eng. Chem. Res.* 35 (1996) 2522.
- [4] D. Yu, M. Aihara, M.J. Antal Jr., *Energy Fuels* 7 (1993) 574.
- [5] S.F. Rice, R.R. Steeper, *J. Hazard. Mater.* 59 (1998) 261.
- [6] T.D. Thornton, P.E. Savage, *AIChE J* 38 (1992) 321.
- [7] S. Gopalan, P.E. Savage, *AIChE J* 41 (1995) 1864.
- [8] T.D. Thornton, E.E. LaDue III, P.E. Savage, *Environ. Sci. Technol.* 25 (1991) 1507.
- [9] T.D. Thornton, P.E. Savage, *Ind. Eng. Chem. Res.* 31 (1992) 2451.
- [10] C.J. Martino, P.E. Savage, *Ind. Eng. Chem. Res.* 36 (1997) 1391.
- [11] S. Gopalan, P.E. Savage, in: K.W. Hutchenson, N.R. Foster (Eds.), *Innovations in Supercritical Fluids: Science and Technology*, ACS Symp. Ser. 608, American Chemical Society, Washington, DC, 1995, p. 217.
- [12] S. Gopalan, P.E. Savage, *J. Phys. Chem.* 98 (1994) 12646.
- [13] E.E. Brock, P.E. Savage, J.R. Barker, *Chem. Eng. Sci.* 53 (1998) 857.
- [14] H.R. Holgate, J.W. Tester, *J. Phys. Chem.* 98 (1994) 810.
- [15] N. Crain, S. Tebbal, L. Li, E.F. Gloyna, *Ind. Eng. Chem. Res* 32 (1993) 2259.
- [16] L. Li, P. Chen, E.F. Gloyna, in: J. Ross (Ed.), *Chemical Oxidation: Technology for the Nineties*, Vanderbilt University, Nashville, TN, 1994.
- [17] M. Krajnc, J.C. Levec, *AIChE J.* 42 (1996) 1977.
- [18] E. Croiset, S.F. Rice, R.G. Hanush, *AIChE J.* 43 (1997) 2343.
- [19] S. Gopalan, P.E. Savage, *J. Phys. Chem.* 98 (1994) 12646.