ELSEVIER

Chemical Engineering Journal 81 (2001) 287–299

Chemical Engineering Journal

www.elsevier.com/locate/cej

Kinetic comparison between subcritical and supercritical water oxidation of phenol

J.R. Portela, E. Nebot, E. Martínez de la Ossa*

Faculty of Sciences, Department of Chemical Engineering, Food Technology and Environmental Technologies,
University of Cádiz, 11510 Puerto Real (Cádiz), Spain

Received 12 May 1999; received in revised form 7 June 2000; accepted 16 June 2000

Abstract

Wet air oxidation (WAO) and supercritical water oxidation (SCWO) processes have been studied by numerous researchers, proving their effectiveness to treat a wide variety of wastes and presenting the kinetics involved in each case. As a result, a substantial amount of kinetic information describing organic reactions in those environments has been accumulated. In most cases, predictions from kinetics models obtained below and above the critical point of water are completely different. Furthermore, predictions from kinetic expressions obtained in the same range of operating conditions vary considerably.

Phenol is a model pollutant that has been the subject of numerous studies both in subcritical and supercritical conditions. In this work, both batch and continuous flow reactors have been used to compare the kinetics obtained for phenol oxidation at subcritical and supercritical conditions. Moreover, most of the rate expressions available in the literature have been compared in order to find the reasons for the discrepancies found. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Wet air oxidation; Supercritical water oxidation; Phenol and kinetics

---

1. Introduction

Hydrothermal oxidation processes have been widely studied and applied to an extensive variety of wastewaters. Aqueous oxidation at high pressure and temperature can be operated at conditions below or above the vapour–liquid critical point of water (374.2°C and 22.1 MPa). The former, known as wet air oxidation (WAO), is typically operated at temperatures and pressures ranging from 200 to 330°C and from 2 to 20 MPa, respectively [1]. The latter, often referred to as super critical water oxidation (SCWO), is carried out at pressures and temperatures above the critical point for pure water, usually ranging from 400 to 650°C and from 25 to 35 MPa, respectively [2].

WAO was first developed and applied as a commercial process by Zimmerman [3,4]. Nowadays, WAO is a well-established technique of importance for wastewater treatment, especially when these are too dilute to incinerate and too toxic to biotreat [5,6]. Since 1960, numerous researchers have studied the kinetics involved in the WAO environment, resulting in some cases a lack of agreement in the parameters obtained for a given organic, i.e. phenol [7].

SCWO is a promising emerging technology, not yet commercially established, useful to eliminate a wide range of problematic wastes from a broad variety of chemical industries. In this way, since the inception of the SCWO process [8], several researchers have proved its effectiveness and have studied the reaction kinetics involved. As a result, a substantial amount of kinetic information describing organic reactions in this environment has been accumulated.

Phenol and substituted phenols are commonly present in industrial wastewaters, even in concentrations of 15,000 ppm [9], and are priority pollutants as they are extremely toxic, even in the parts per billion range [10]. For those reasons, phenol has been the subject of numerous studies both in subcritical and supercritical conditions. Current state of knowledge has been condensed in Table 1. As can be seen, there is a considerable variation in the kinetic parameters obtained. However, it is important to point out that variation in global reaction orders can be expected when the reaction conditions change. Moreover, Arrhenius parameters are very sensitive to the reaction orders, experimentally obtained or assumed, in the rate law. For those reasons, since different authors have studied a different set of conditions, published kinetic for the same organic may be different.

---

* Corresponding author. Tel.: +34-956-016378; fax: +34-956-016411.
E-mail address: enrique.martinezdelaossa@uca.es (E. Martínez de la Ossa).

PII: S1385-8947(00)00226-6

Nomenclature

A	pre-exponential factor in Arrhenius equation ($l^{a+b+c-1}$ $mol^{1-a-b-c}$/s)
$[O_2]$	concentration of oxygen (mol/l)
[Phenol]	concentration of phenol (mol/l)
$[H_2O]$	concentration of water (mol/l)
E_a	activation energy (J/mol, unless stated as kJ/mol)
k'	pseudo-first-order kinetic constant (l/s)
a	reaction order with respect to phenol
b	reaction order with respect to oxygen
c	reaction order with respect to water
R	gas constant (J/mol K)
T	temperature (K, unless stated as °C)
t	reaction time (s)
t_I	induction time (s)
τ	reactor residence time (s)
X	conversion (%)
TOC	total organic carbon (mg/l)

Subscript

o	initial value

Nevertheless, different global rate laws should predict similar results (reaction rates or conversions) for a given set of conditions, at least in the range where those studies were carried out. We have found that global rate expressions are often mainly suitable to describe those experiments that were carried out to obtain the kinetic parameters, appearing a lack of reproducibility from one study to another. There are many aspects like non-isothermal operation, different geometry and material of the reactor, operating procedures, different set of conditions, mathematical treatment of the data, etc., that can lead to a disagreement in model predictions [11].

Those variations in model predictions become even more complex when comparing subcritical and supercritical results. Should the same kinetics be applicable when the critical point of water is crossed? In order to clarify that question, phenol has been chosen as a model pollutant in this work, comparing both subcritical and supercritical kinetics in both batch and continuous flow reactors.

In a previous work, we studied the oxidation of phenol in the subcritical range [7]. In this work, a continuous flow reactor has been used to obtain experimental data at supercritical conditions, and to compare our results with those that appear in the literature.

Table 1
Kinetic data in the literature for non-catalytic aqueous oxidation of phenol. Parameters a, b, c, A and E_a correspond to Eq. (3).

Phenol concentration (mg/1)	Temperature range (°C)	Pressure (MPa)[a]	Oxygen Source	Oxygen Excess (%)	Reactor Type	a	b	c	A ($l^{a+b+c-1}$ $mol^{1-a-b-c}$/s)	E_a (kJ/mol)	Reference
WAO											
1400–8900	180–210	0.5–3.5 (“)	O_2	NA	batch	1	1	0	$10^{9.29}$	107	[34]
NA	90–180	NA	O_2	NA	NA	1	0.5	0	NA	175	[33]
1400–3000	200–250	5.5–15	Air	NA	flow	1	1	0	$10^{4.93}$	45	[25]
2500–10000	185–230	10.4–15.6 (“)	O_2	NA	NA	1	0–1	0	NA	20	[38]
5000	204–260	2–2.5 (“)	O_2	NA	batch	1	NA	0	NA	33	[5]
10–100	175–220	9.3 (“)	O_2	NA	NA	1	0	0	$10^{8.42}$	93	[30]
1000	140–180	2.6–5	O_2	NA	NA	1	1	0	$10^{5.52}$	56.6	[31]
140–154	130–200	13.8	Air	NA	NA	1	0.5	0	$10^{12.05}$	112	[35]
200	150–195	0.3–1.0	O_2	NA	NA	1	0.5	0	$10^{8.97}$	93	[36]
200	150–180	0.3–1.1 (“)	O_2	NA	batch	1	1	0	$10^{4.86}$	50	[32]
1000	170–230	2.9–3.9	O_2	NA	NA	1	1	0	$10^{8.65}$	113.3	[29]
940	145–210	2–4.5	Air	NA	batch	1	1	0	$10^{9.82}$	92	[11]
340–1390	150–300	10–20	Air	750–1500	batch	1	0	0	$10^{1.58}$	34	[7]
SCWO											
100–400	284–429	29–34	O_2	NA	flow	1	1	0	$10^{5.42}$	63.8	[37]
3–37	420–480	27	O_2	>200	flow	0.85	0.5	0.42	$10^{2.34}$	51.8	[28]
3–37	420–480	27	O_2	50–400	flow	1.09	1.23	−0.05	$10^{14.7}$	176.4	[27][b]
500–1000	380–450	23–26.5	H_2O_2	50–1000	flow	1	0.4	–[d]	$10^{8.69}$	124.7	[21]
828	380–440	19–27	O_2	0–1750	batch	1	–[c]	1.38	$10^{4.95}$	99.6	[24]
0.5–12.2	370–430	25.6–33.7	O_2	200–900	flow	1	0.48	−0.45	$10^{4.45}$	50.4	[23]
50–593	400–500	25	H_2O_2	100–475	flow	1	0	0	$10^{1.35}$	39.2	This Work

[a] Total pressure, unless marked with (“) for oxygen partial pressure.
[b] based on an elementary reaction model.
[c] Langmuir-type equation with the ratio of oxygen to phenol concentration was adopted.
[d] an equation considering reaction molar volume is included in the rate law.
NA not available.

2. Experimental apparatus and procedure

Oxidation reactions were accomplished in both batch and flow reactors. The batch reactor, only used in the subcritical range, was a 316 stainless steel 300 ml autoclave manufactured by Autoclave Engineers, fitted with a variable speed ‘Magnedrive’ stirrer and an electric furnace. The reactor was initially charged with 100 ml of deionised water, pressurised with air and heated until desired reaction conditions. Aqueous solutions of phenol were then injected into the reactor to start the oxidation process. Liquid samples were withdrawn periodically and analysed in order to follow the oxidation progress. More specific details of the equipment and experimental procedures are well described in a previous work [7].

The flow reactor operated both at sub- and super-critical conditions. Fig. 1 shows a schematic diagram of the laboratory-scale, continuous flow reactor system. All wetted parts, from the pumps to the back-pressure regulator, were made of stainless steel 316. The reactor was constructed from a 2.5 m length of 1/4 in. o.d. tubing. The oxidant feed stream was prepared by dissolving hydrogen peroxide into deionised water in one feed tank. Another feed tank was loaded with an aqueous solution of phenol. The two feed streams were pressurised in two different lines by two high-pressure metering pumps and then separately preheated. In order to assure that all H_2O_2 is decomposed to give H_2O and O_2, two in series preheating systems were used for the oxidant feed stream: (1) by flowing through 3 m coiled 1/8 in. o.d. tubing electrically heated and (2) by flowing through 5 m of coiled 1/8 in. o.d. tubing submerged in a fluidised sand bath (Techne Model SBL-2). Based on the studies of Croiset et al. [12], it has been evidenced that H_2O_2 completely decomposed in the preheaters even in those experiments carried out at high flow rate and low temperature. Organic feed stream was preheated by flowing through 3 m coiled 1/8 in. o.d. tubing submerged in the fluidised sand bath.

After preheating, the two lines were mixed at the reactor entrance. Thermocouples were installed at the joint between the two coil sections, at the reactor inlet and outlet. Typically, the difference between the upstream and downstream fluid temperatures was ±3°C, and always <±5°C. The average of these two temperatures was used as the reaction temperature. Upon exiting the reactor, the effluent was cooled rapidly in a counter current heat exchanger and afterwards, the system pressure was reduced by using a back-pressure regulator. The product stream was then separated into liquid and vapour phases.

To start an experiment, both the organic and oxidant feed pumps were started using distilled and deionised (DDI) water as feed. The fluidised sand bath was then heated up to the desired temperature. After the pump flow rates, reactor pressure and temperature stabilised, the feed pump inlets were switched to the feed solutions. In the hydrolysis/pyrolysis

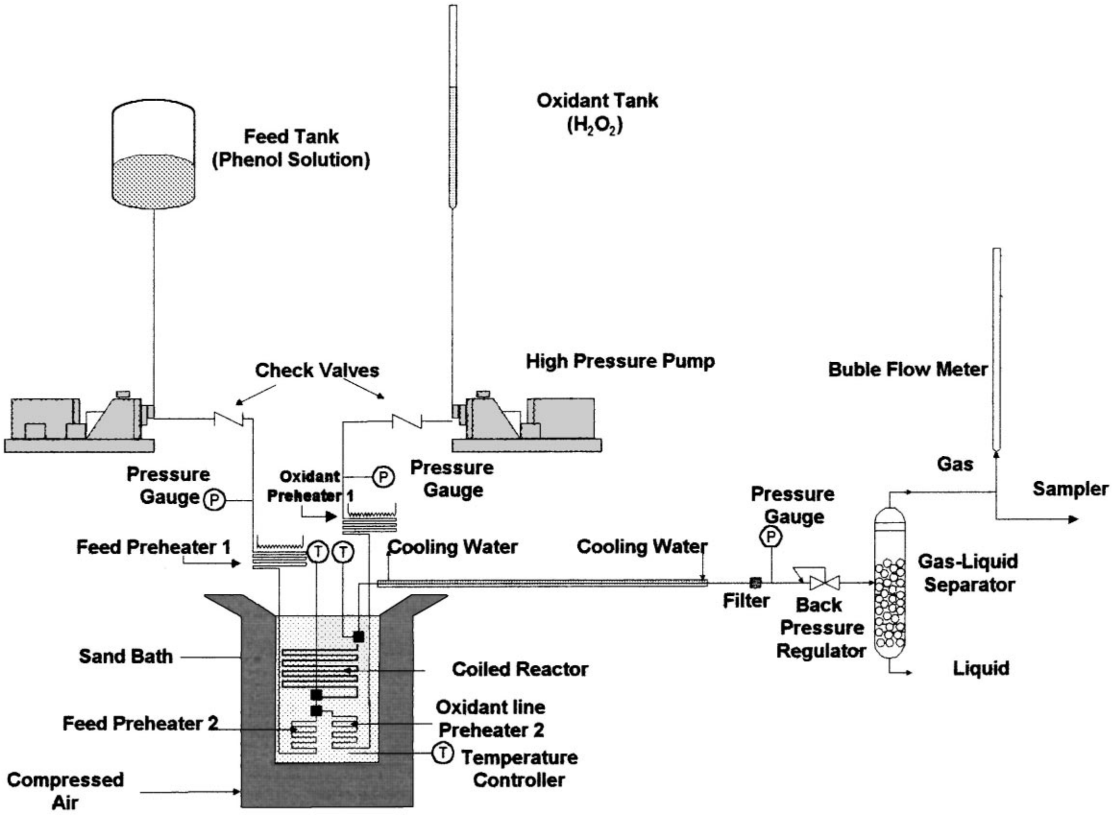

Fig. 1. Schematic diagram of the continuous-flow reactor system.

experiments, the oxidant tank contained only DDI water and was purged with N_2. Typically, the reactor system was allowed to stabilise for about 15 min after that switch. Flow rates for the oxidant and organic feed streams ranged from 10 to 30 ml/min and from 4 to 9 ml/min, respectively. The flow rates were measured repeatedly using graduated vessels and a stopwatch until a steady-state condition was reached. The duration of each flow measurement was typically about 2 min. The accuracy of the volumetric flow measurement was within ±2%. Pressure was fixed at 25 ± 0.3 MPa. Temperatures ranged from 300 to 500°C. Reactor residence times were calculated from the density of water at the experimental conditions, reactor volume, and the total feed flow rate.

3. Materials and analytical methods

Phenol (Panreac, 99% pure) and hydrogen peroxide (Panreac, 30% w/v aqueous solution) were used. Dilutions of these feed stocks solutions for preparing feed solutions of required concentrations were made using DDI water.

A Perkin-Elmer (Autosystem) gas chromatograph equipped with a Flame Ionisation Detector was used to analyse the phenol content. A 30 m length and 0.25 mm diameter capillary column Nukol (SUPELCO) was used, keeping the furnace temperature at 180°C for phenol determination.

A five level calibration method (from 10 to 2000 ppm) with external standard was used to calibrate the phenol analysis method, obtaining a correlation coefficient of 0.999.

Gas samples were analysed on a Konik 2000 gas chromatograph with a Thermal Condutivity Detector and a 2 m Carbosieves II (SUPELCO) packed column. A temperature ramp from 55 to 150°C (at 30°C/min) was used to separate the O_2 from CO_2, and other possible gases (CO, NO_x). The system was calibrated with a standard gas mixture containing H_2, N_2, CO_2 and CH_4.

Total organic carbon (TOC) contents of liquid samples were monitored. The analysis was performed according to Standard Method 5310C [13] and using a TOC analyzer Shimadzu, Model 5050. Multiple injections were made for all samples to establish the reproducibility of the results.

4. Results and discussion

In agreement with the literature, none of the pyrolysis/hydrolysis experiments showed any degradation of phenol in the conditions studied, so in oxygen absence, phenol is not thermally destroyed. Therefore, in the oxidation experiments, there is no other competing reaction. In all cases, oxygen was always in great excess in comparison to the stoichiometric oxygen concentration needed to the complete phenol oxidation to carbon dioxide and water.

4.1. Reaction kinetics obtained in the subcritical range

From the experiments carried out in a batch reactor in our previous work [7], a kinetic equation was put forward for phenol wet air oxidation, covering the range of temperatures (150–300°C) and pressures (10–20 MPa). At those temperatures, the presence of an induction period, in which there is very little or no measurable change in phenol concentration, is well established. In this way, the kinetic equation has a term for the induction period and another one for the oxidation phase. The oxidation term was found only temperature dependent but the induction term is pressure and temperature dependent.

The integrated form of the proposed pseudo-first-order kinetic equation was

$$\ln\frac{[\text{Phenol}]}{[\text{Phenol}]_\text{o}} = k'(t - t_\text{I}) \tag{1}$$

and

$$k' = A\exp\left(-\frac{E_\text{a}}{RT}\right) \tag{2}$$

where [Phenol] is phenol concentration (subscript ‘o’ denotes ‘initial’), t and t_I are reaction time and induction time (s), respectively, k' the pseudo-first-order rate constant, A the pre-exponential factor (found as 38.4 ± 11.6/s), E_a the activation energy (found as 34,400 ± 9900 J/mol), R the universal gas constant (8.314 J/mol K), and T is the temperature (K).

As can be seen in Fig. 2, the predicted curve from the batch model agrees with the experimental data obtained in this work by using the continuous flow reactor and with those data published by other researchers [14–17], within the range of WAO operating conditions.

4.2. Reaction kinetics obtained in the supercritical range

Experimental conditions, initial values of phenol and oxygen concentrations, and phenol and TOC conversions of each experiment are presented in Table 2. Phenol and TOC concentrations at the reactor inlet were calculated from the feed stock concentrations and pump flow rates.

The global rate for phenol destruction may be expressed as

$$\text{rate}=\frac{\text{d[Phenol]}}{\text{d}t} = A\exp\left(-\frac{E_\text{a}}{RT}\right)[\text{Phenol}]^a\,[\text{O}_2]^b\,[\text{H}_2\text{O}]^c \tag{3}$$

where a, b, and c are the reaction orders of phenol, oxygen, and water, respectively. The reaction rate coefficient is expressed in Arrhenius form.

Eq. (3) considers that water can actively participate in the reactions implied and it is not merely an inert medium for oxidation reactions, as was found by Helling and Tester [19] and Rofer and Streit [20]. On the other hand, some authors

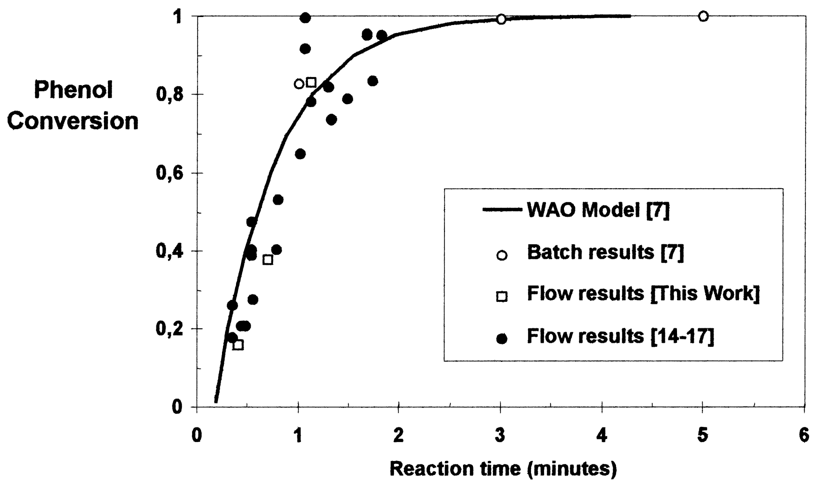

Fig. 2. Comparison between predicted curve from WAO of phenol [7] and experimental data at 300°C: (○) from batch reactor [7]; (□) from flow reactor (this work) and (●) from flow reactor in the literature [14–17].

Table 2
Summary of phenol oxidation experiments conducted in the flow reactor

T (°C)	Reaction time (s)	O_2 excess (%)	[Phenol] (mg/l)[a]	X_{Phenol} (%)	Final TOC (mg/l)	X_{TOC} (%)
300	24.6	74	593	15.7	–[b]	–[b]
300	41.8	11	346	37.7	–[b]	–[b]
300	67.7	172	565	82.9	350.2	39.7
380	14	40	400	26.4	–[b]	–[b]
380	15.7	155	220	27.4	592.4	0
380	16.6	207	199	24.6	335.2	0
380	18.4	76	245	20.5	–[b]	–[b]
380	22.4	159	221	40.9	567.2	0
380	22.5	190	201	32.2	323.2	6.9
380	35.7	193	200	59.5	278.7	18.1
380	38.3	153	345	82.3	383.0	34.7
380	49.4	204	199	82.7	215.7	36.4
400	8.4	96	86	15.8	381.5	1.6
400	9.6	258	88	22.7	361.4	5.9
400	11.1	147	82	24.1	–[b]	–[b]
400	13.1	153	81	25.3	343.8	6.6
400	18.0	173	80	27.4	340.6	6.7
400	18.8	223	96	28.7	372.9	10.6
420	4.0	98	70	13.0	–[b]	–[b]
420	6.0	141	33	14.2	–[b]	–[b]
420	8.0	240	90	16.7	450	0
420	11.3	183	92	17.2	–[b]	–[b]
425	13.0	327	91	25.5	536.3	1.7
420	13.2	315	79	19.0	448.7	3.2
420	21.1	240	92	25.1	514.7	4.7
425	23.4	257	103	31.5	613	1.4
450	7.0	335	63	23.2	386	1.7
450	11.6	473	60	34.4	321	14.4
450	16.5	476	60	43.2	301.5	19.0
475	5.8	415	61	13.8	478	0
475	10.3	341	68	35.6	480	9.9
475	16.5	318	71	46.2	410	26
500	5.3	465	50	17.9	452.3	8.6
500	9.5	395	56	37.6	424.3	22.4
500	14.9	300	67	52.9	379.7	34.7

[a] Initial phenol concentration at operating conditions.

[b] Not available.

have assumed that water does not participate appreciably in the oxidation reaction [21,37], in agreement with the latest findings of Gopalan and Savage [22]. Furthermore, negative orders for water can also be found in the literature [23]. As a result, it can be concluded that the dependence on the H_2O concentration is not yet understood. The possible effects of solvent on reaction rate has been extensively explained by Koo et al. [24], concluding that it cannot be explained by phase behaviour, solvation, electrostatic or transition state theory. Water seems to participate in the reaction as a reactant via a multi-step reaction mechanism. Since the reaction medium always consisted of more than 99% of water, we consider that its impact on the phenol disappearance rate, if any, may be hidden. In other words, our set of experiments were not designed to evaluate the effect of water concentration. In this way, we considered zero the reaction order for water.

In order to determine the global kinetic parameters for phenol oxidation in supercritical water, Eq. (3) has been expressed as follows:

$$\begin{aligned}\ln(\text{rate}) &= \ln\left(-\frac{\mathrm{d}\,[\text{Phenol}]}{\mathrm{d}t}\right)\\ &= \ln A - \frac{E_a}{RT} + a\ln[\text{Phenol}] + b\ln[O_2] \qquad (4)\end{aligned}$$

A multiple linear regression (sum of squared differences method) of experimental data to Eq. (4) was performed. Experimental values of rate of phenol destruction must be estimated before performing the regression. That estimation was made in two steps. (1) The evolution of the normalised phenol concentration ($[\text{Phenol}]/[\text{Phenol}]_o$) versus reaction time was fitted by an exponential function. (2) Experimental rate values were estimate by derivation of the expressions obtained in the first step. Table 3 shows fitted expressions used to estimate experimental rate values.

Estimated kinetic parameters from multiple linear regression are given in Eq. (5). As can be seen, phenol order was found close to the unity, in agreement with the literature. No dependence of oxygen concentration was found, which does not agree with those obtained in the literature (around 0.3–0.5) but makes sense due to the great oxygen excess present in all experiments (usually oxygen to phenol molar ratio >21, being, in most cases, phenol and TOC conversion under 40 and 15%, respectively).

$$\text{rate} = 10^{2.26\pm2.22}\exp\left(-\frac{55200\pm16900}{RT}\right)[\text{Phenol}]^{0.95\pm0.41}\,[O_2]^{-0.03\pm0.26} \qquad (5)$$

Even though kinetic parameters obtained by multiple linear regression seem to be valid qualitatively, there is a big uncertainty associated with them, and Eq. (5) will not be used to describe the kinetics involved.

Since the overall reaction appears to be approximately first-order, pseudo-first-order model have been performed. An Arrhenius plot for pseudo-first-order constants is shown in Fig. 3, and kinetic parameters obtained are presented in Eq. (6).

$$\text{rate} = 10^{1.34\pm0.77}\exp\left(-\frac{39200\pm10700}{RT}\right)[\text{Phenol}] \qquad (6)$$

Similarly, as shown in Fig. 4, the predicted phenol conversions compares favourably with the experimental data. Only two data displayed a considerable discrepancy in phenol conversions. However, subtracting these data from the regression did not show a significant effect on the modelling results. In this way, Eq. (6) is a simple and valid expression to represent our experimental data.

4.3. Kinetic comparison

In order to compare all rate law expressions available in the literature, Eqs. (7) and (8) have been used to calculate the conversion predicted by different authors.

$$X = 1 - \left(1-(1-a)A\exp\left(\frac{E_a}{RT}\right)\tau[\text{Phenol}]_0^{a-1}\,[O_2]_0^b\,[H_2O]_0^c\right)^{1/(1-a)}, \quad \text{for } a \neq 1 \qquad (7)$$

$$X = 1 - \exp\left(-A\exp\left(-\frac{E_a}{RT}\right)\tau[O_2]_0^b\,[H_2O]_0^c\right), \quad \text{for } a = 1 \qquad (8)$$

where X is the conversion of phenol, and τ the reactor residence time. The concentration subscript 0 represents values at the reactor entrance.

Eqs. (7) and (8) are obtained by integration of the plug-flow reactor design equation using the global rate law presented in Eq. (3) and the definition of conversion. The oxygen and water concentrations are assumed constant throughout the reaction.

All kinetic comparisons have been made by using reported kinetic parameters shown in Table 1 and a fixed set of operating conditions. In other words, for a given temperature, pressure and phenol, oxygen and water concentrations, Eqs. (7) or (8) have been used to calculate predicted conversions (calculated from the rate laws) from different authors.

Table 3
Fitted expressions for normalised phenol concentration ($[\text{Phenol}]/[\text{Phenol}]_o$) vs. reaction time at different temperatures

Temperature (°C)	Fitted equation for $[\text{Phenol}]/[\text{Phenol}]_o$ vs. t	r^2
400	$\exp(-0.0195t)$	0.96
420	$\exp(-0.0241t)$	0.94
450	$\exp(-0.0353t)$	0.99
475	$\exp(-0.0379t)$	0.98
500	$\exp(-0.0492t)$	0.99

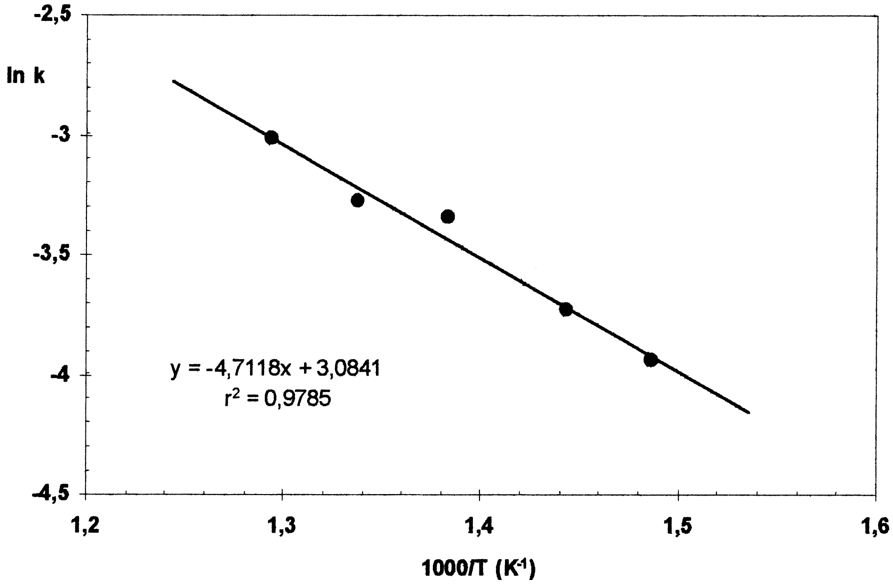

Fig. 3. Arrhenius plot for SCWO of phenol (pseudo-first-order model).

This type of comparison is valid, provided the oxygen concentration can be considered constant, since Eqs. (7) and (8) are based on that assumption. Another test of consistency for different studies is to calculate predicted reaction rates by Eq. (3), where there is no requirement for oxygen excess. So, in those cases where no oxygen excess is considered, Eq. (3) has been used to compare reaction rates predicted by different authors.

Three different comparisons have been made in this work: (a) different studies in the subcritical region; (b) different studies in the supercritical region and (c) differences between subcritical and supercritical kinetics.

4.3.1. Subcritical region

Generally, a great disagreement have been found among the predictions made by different authors. Within the range of operating conditions typically used for WAO of phenol, different results have been obtained. (1) Considering an initial phenol concentration of 500 mg/l, stoichiometric oxygen concentration and a temperature of 180°C, it is possible to find some agreement among reported rate laws. Fig. 5 shows the results obtained by using Eq. (3). (2) However, if we consider an initial phenol concentration of 800 mg/l, three times the stoichiometric oxygen concentration and a temperature of 200°C, there is a great disagreement among

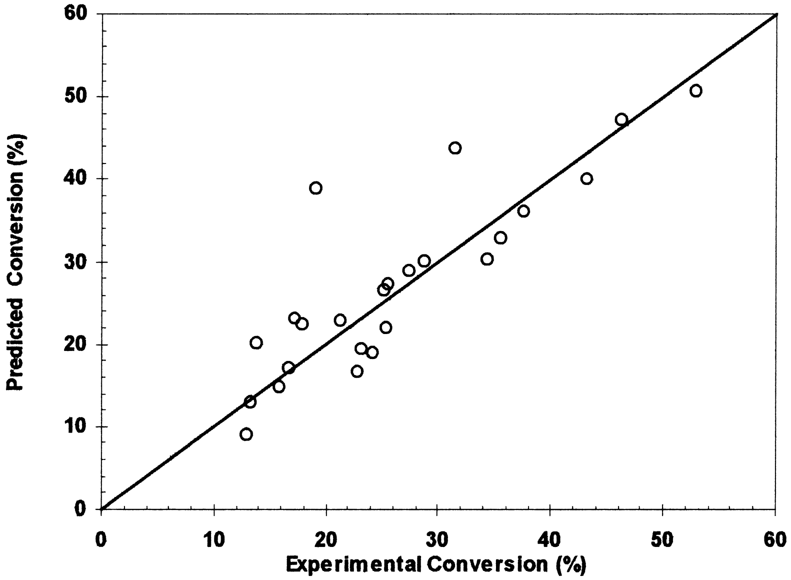

Fig. 4. Predicted vs. experimental conversions for phenol oxidation.

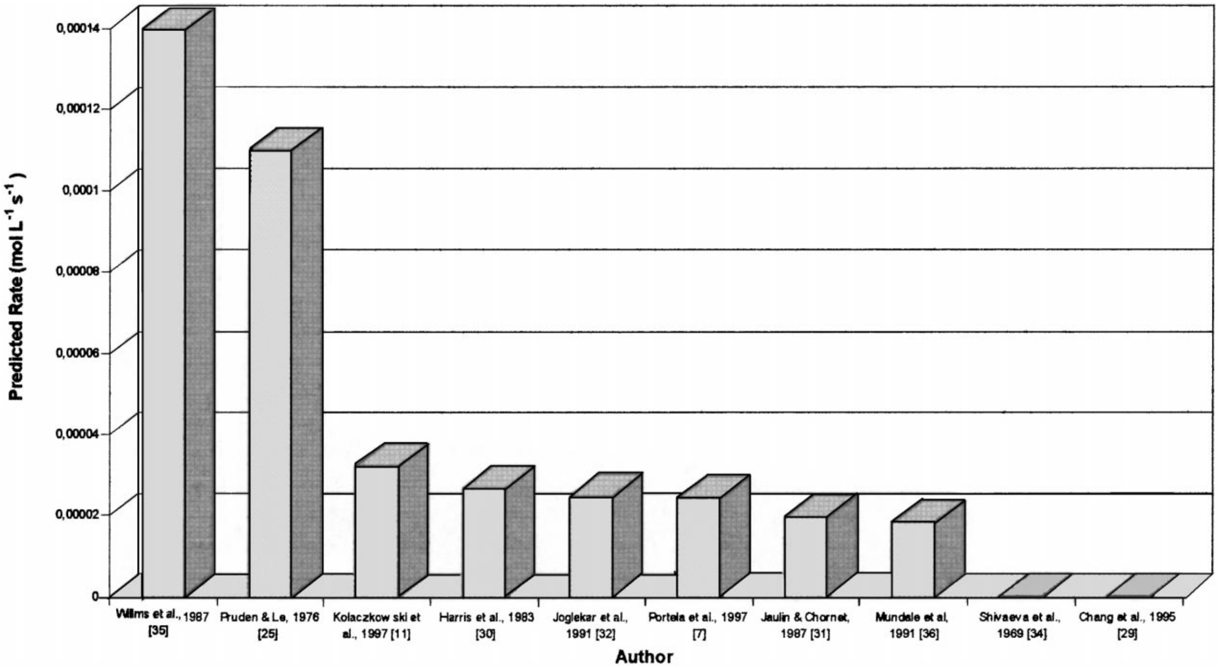

Fig. 5. Predicted reaction rates from different WAO studies by using Eq. (3) and phenol concentration 500 mg/l, stoichiometric oxygen and a temperature of 180°C.

different studies. Fig. 6 shows different predicted conversions calculated by using Eq. (8). As can be seen, different kinetic coefficients present in Table 1 can lead to an agreement or disagreement among different authors if operating conditions change slightly.

As Kolaczkowski et al. [11] stated, the differences among rate laws reported for WAO of phenol can be the result of some aspects of difficulty in the estimation of global WAO rate constants. (a) Global rate constants can change according to the mechanism of phenol destruction; therefore, depending on the reaction conditions, the relative contribution of each of all elemental reactions among a number of different species (e.g. oxygen, hydroxyl radical, etc.) can change. (b) For WAO operation conditions, saturated oxygen concentration varies considerably with both partial pressure and temperature. (c) Geometry and nature of the reactor may

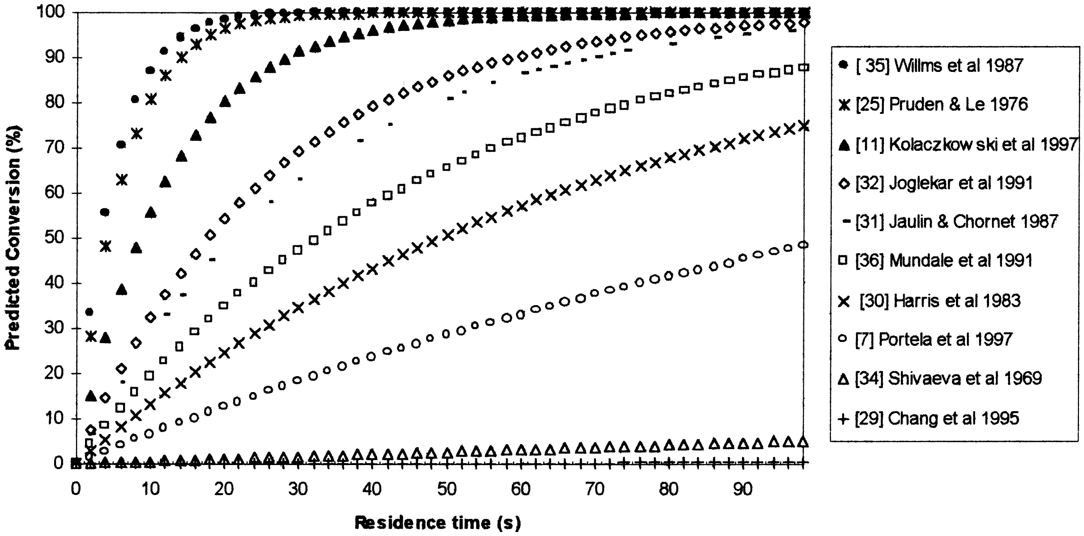

Fig. 6. Predicted conversions from different WAO studies by using Eq. (8) and phenol concentration 800 mg/l, three times stoichiometric oxygen and a temperature of 200°C.

play a role in the oxidation rate, since phenol oxidation is assumed to follow a radical mechanism. (d) The repartioning of volatile species between the vapour and liquid phases can lead to errors in the results (however, this effect is minimal in the case of phenol due to its low volatility). (e) Other sources of errors are unpredictable (sampling procedures, impurities, mathematical treatment, etc.). As an example, Tufano [18] reanalysed the data of Thornton and Savage [14] and found a quite lower value for the activation energy (12 kJ/mol), although the partial orders were found only slightly different.

It is important to point out that even though variations in E_a are important, no value between 63 and 92 kJ/mol have been reported. Moreover, pre-exponential factors found by different authors vary extremely contributing to the variations observed in Fig. 6. The existence of two groups of E_a values, namely, 20–63 and 92–124 kJ/mol, suggests two different behaviours for phenol oxidation under hydrothermal conditions. Pruden and Le [25] proposed that shorter activation energies could be characteristic of total oxidation to carbon dioxide and water, while the greatest values are probably the result of polymerisation reactions under conditions near the stoichiometric ratio of oxygen/phenol and under conditions of phenol excess. As Devlin and Harris proposed [26], the mechanism of the oxidation of aqueous phenol with dissolved oxygen varies as the ratio of phenol/oxygen goes from excess oxygen to excess phenol. So, under conditions of oxygen excess, intermediate ring compounds, dihydric phenols and quinones were not observed. These explanations agree with the activation energy resulting from our experiments (around 30–40 kJ/mol), where no experiment was carried out under oxygen defect.

4.3.2. Supercritical region

In this case, better agreement have been found among the predictions made by different authors. However, within the range of operating conditions typically used for SCWO of phenol, two different situations can be observed. (1) Considering an initial phenol concentration of 50 mg/l, three times stoichiometric oxygen concentration and a temperature of 400°C, it is possible to find a very good agreement among five different studies. Fig. 7 shows the results obtained by using Eqs. (7) or (8). (2) However, if we consider an initial phenol concentration of 100 mg/l, two times the stoichiometric oxygen concentration and a temperature of 420°C, there is a considerable disagreement among different rate laws. Fig. 8 shows different predicted conversions calculated by using Eqs. (7) or (8).

It is important to point out that power-law rate expressions can be only considered as equations that describe the general trend of experimental data, but they do not describe at all any detail of the complex oxidation chemistry. In this way, the activation energy obtained is not the intrinsic one and it can only be considered as a parameter that predicts the temperature dependence of the phenol disappearance rate in the range studied. Furthermore, global reaction orders obtained are only suitable for the reaction conditions used in the kinetic study. Moreover, kinetic parameters obtained from power-rate law expressions have a bit of uncertainty associated with them, and must be used with caution.

Within all fitting parameters in a power rate law, the reaction orders have a critical importance, so the set of conditions selected in the kinetic study will limit the use of the expression obtained. In other words, if a set of experiments

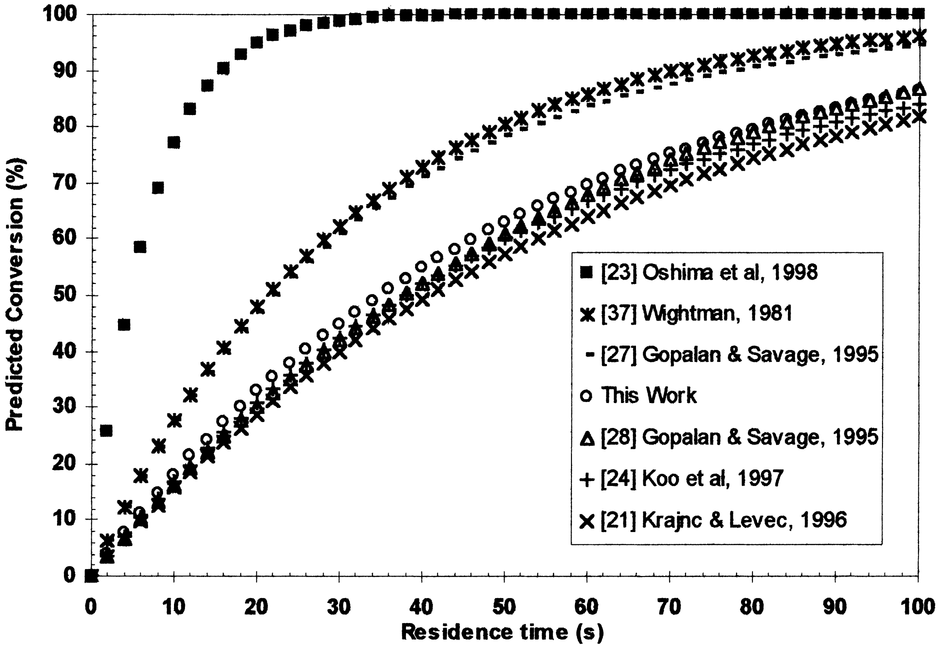

Fig. 7. Predicted conversions from different SCWO studies by using Eqs. (7) and (8) and phenol concentration 50 mg/l, three times stoichiometric oxygen and a temperature of 400°C.

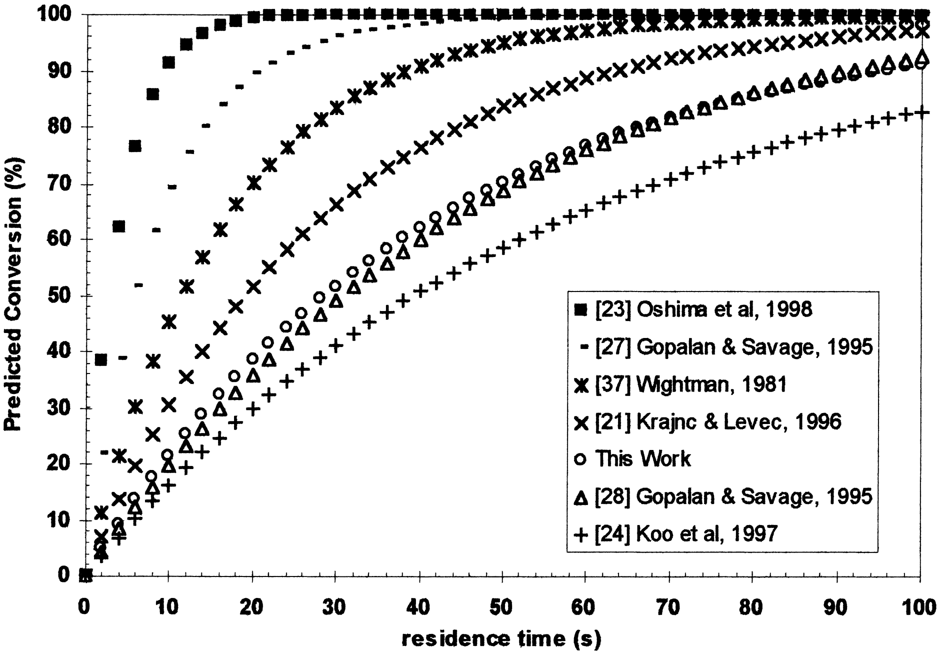

Fig. 8. Predicted conversions from different SCWO studies by using Eqs. (7) and (8) and phenol concentration 100 mg/l, two times stoichiometric oxygen and a temperature of 420°C.

is carried out without oxygen excess, the resulting reaction order respect to oxygen (b) will be approximately 1. On the other hand, if a great oxygen excess is used, reaction order *b* will be nearly zero. Different experiments in both situations will be probably well described if its appropriate reaction order is used in the rate law expression. However, if the kinetic study includes all oxygen concentrations, from defect to oxygen excess, probably the resulting reaction order for oxygen will be around 0.5 and the power law rate expression will not predict adequately those experiments with oxygen concentrations in the extremes of the range used.

As a result, it is obvious that the usefulness of a power rate law expression is very limited, even in the range where it was obtained. As an example, the rate law expression proposed in this work will only describe the SCWO of phenol under oxygen excess and its use in any other range will probably lead to a disagreement with experimental observations.

As a test of consistency, the rate law proposed in this work from SCWO of phenol (Eq. (6)) has been used to predict the results from the literature. Fig. 9a shows a comparison between experimental data from the studies carried out in a continuous flow reactor at the University of Michigan [14–17,28] and predicted conversions by our model. We have chosen the data from the University of Michigan group because of their thorough work on the kinetics of phenol oxidation in supercritical water and also because they publish all raw data needed.

As can be seen in Fig. 9a, our model predictions generally underestimate the experimental data, mainly for high conversions. Most of the data in disagreement correspond to experiments in near critical region (380°C) (represented by empty circles). In that range, due to the proximity of the critical point, water properties differ from the subcritical and the supercritical range and are very sensible to small changes in the operation conditions, leading to a great scatter in experimental data. However, those experiments carried out at temperatures in the range 400–480°C and oxygen excess (represented by filled circles) are better described by the rate law expression proposed in this work.

Similar tests of consistency have been tested by using other reported rate laws expressions for SCWO of phenol. As can be seen in Fig. 9b, a parity plot for experimental conversions from University of Michigan and predicted conversions from their own power rate law expression [28] lead to a good agreement. However, the use of other rate law expressions lead to a general over-prediction of experimental conversions, as shown in Fig. 9c, d and e.

On the other hand, rate laws from different authors have been used to predict the results of our own experiments. Again, a great disagreement has been found, resulting the best agreement when the rate law from Gopalan and Savage [28] is used. Fig. 10 shows this parity plot.

4.3.3. Differences between subcritical and supercritical kinetics

Subcritical and supercritical water oxidation of phenol can be considered, to a certain extent, as the same process. In both cases, water, oxygen and phenol are the chemicals present, and a free radical mechanism is accepted. The main difference is the existence of two phases in the subcritical range and only one phase at supercritical conditions. However, if operating conditions in the subcritical range

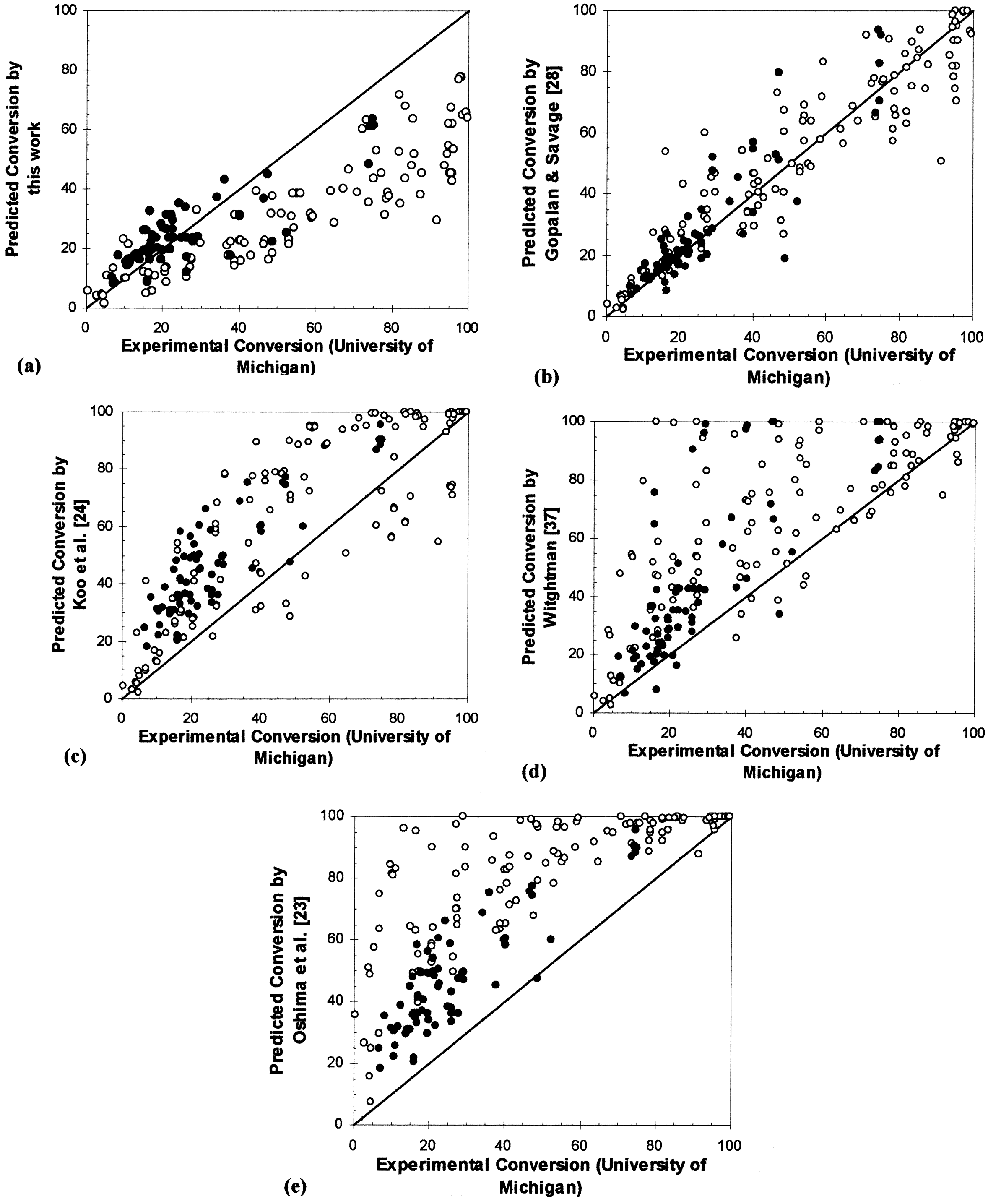

Fig. 9. Comparison between experimental conversions from different studies at the University of Michigan [14–17,28] and predicted conversions by different rate laws in the literature. (a) This work. (b) Gopalan and Savage [28] (c) Koo et al. [24] (d) Wightman [37] (e) Oshima et al. [23]. (○) Data from experiments carried out at 300–380°C. (●) Data from experiments carried out at 400–480°C (most experiments were carried out under oxygen excess).

are selected in order to eliminate mass transfer limitations, that difference becomes minimal. Furthermore, the effect of pressure itself can be considered insignificant in the ranges typically used [24].

If the reasoning outlined above can be considered valid, the same kinetic model should be applicable in the whole range of operating conditions. Reported kinetic parameters (Table 1) for subcritical and supercritical water oxidation of phenol have been compared each other by using Eq. (3). We have found that whatever the phenol, oxygen and water concentrations used, predicted reaction rates from WAO studies are always in disagreement with those predicted by SCWO

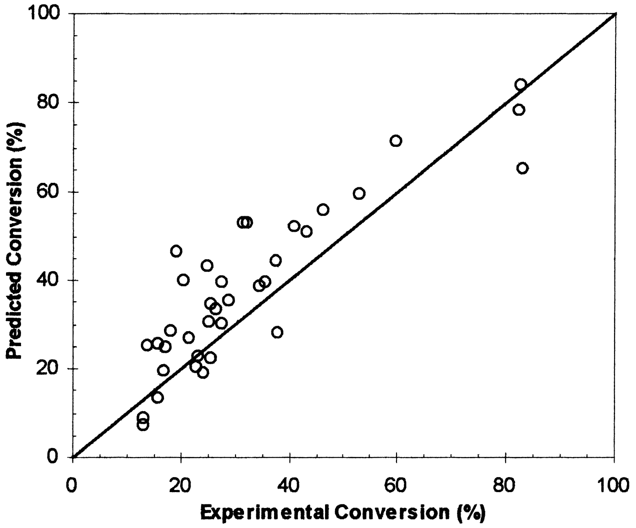

Fig. 10. Comparison between experimental conversions from this work and predicted conversions by Gopalan and Savage [28].

studies. Curiously, for a given temperature, below or above the critical point for pure water, reaction rates predicted by WAO studies are always higher than those predicted by SCWO studies, and any coincidence observed must be considered fortuitous. This again confirms that power rate law expressions are only applicable within the range where they were obtained.

In order to avoid the limitations related to global rate laws, the use of detailed mechanisms based on studies for hydrothermal oxidation would be the logical solution. Since those complex mechanism have not been studied yet, Gopalan and Savage [27] developed a detailed free-radical mechanism based on gas-phase chemistry to model the supercritical water oxidation of phenol, resulting an activation energy and oxygen reaction order higher than those determined experimentally. They assume that this first attempt at mechanistic modelling used several simplifying assumptions and an improvement is needed in future models.

5. Conclusions

Simple kinetic equations (based on pseudo-first-order assumption) for WAO and SCWO of phenol predict reasonably well the conversions observed experimentally in this work and those obtained by other authors, as long as the operating conditions are in the same range. In the supercritical region, the rate law from Gopalan and Savage [28] provided the best match with our results.

Observing the kinetic parameters obtained in this work and those present in the literature, it is not possible to predict the real behaviour of phenol oxidation under hydrothermal conditions. There are many aspects, like oxygen/phenol ratio, different geometry and material of the reactor, operating procedures, etc., that affects the reaction mechanism and, consequently, the resulting rate law expression.

Global rate laws obtained in WAO and SCWO environments are mainly useful for the operating conditions where they were obtained, and many times only applicable to the reactor system in which experimental data were obtained. At near critical operating conditions, experimental data are scattered and difficult to predict from WAO or SCWO rate law expressions. Furthermore, predicted reaction rates from WAO studies are always higher than those predicted by SCWO studies and any coincidence observed must be considered fortuitous.

References

[1] V.S. Mishra, V.V. Mahajani, J. Joshi, Wet air oxidation, Ind. Eng. Chem. Res. 34 (1995) 2–48.
[2] E.F. Gloyna, L. Li, Supercritical water oxidation for remediation of wastewaters and sludges, in: R.A. Meyers (Ed.), Encyclopedia of Environmental Analysis and Remediation, Wiley, New York, 1998.
[3] F.J. Zimmerman, New waste disposal process, Chem. Eng. (1958) 117–120.
[4] F.J. Zimmerman, D.G. Diddams, The Zimmerman process and its application to the pulp and paper industry, Tappi 43 (1960) 710.
[5] C.R. Baillod, R.A. Lamporter, B.A. Barna, Wet oxidation for industrial waste treatment, Chem. Eng. Progress 3 (1985) 52–55.
[6] M.A.G. Vorstman, M. Tels, Wet air oxidation of toxic wastewater, in: Proceedings of the Second European Conference, Environ. Technol. (1987) 247–55.
[7] J.R. Portela, J. Bernal, E. Nebot, E. Martinez de la Ossa, Kinetics of wet air oxidation of phenol, Chem. Eng. J. 67 (1997) 115–121.
[8] M. Modell, Supercritical water oxidation, in: H.M. Freeman (Ed.), Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw-Hill, New York, 1989, pp. 8–153.
[9] J.A. García-Portilla, F.V. Diez, J. Coca, Métodos alternativos para el tratamiento de efluentes fenólicos industriales, Ingeniería Química 238 (1989) 151–158.
[10] U.S. Kulkarni, S.G. Dixit, Destruction of phenol by oxidation with SO_3^{2-}–O_2, Ind. Eng. Chem. Res. 30 (1991) 1916–1920.
[11] S.T. Kolaczkowski, F.J. Beltran, D.B. McLurgh, F.J. Rivas, Wet air oxidation of phenol: factors that may influence global kinetics, Trans. IChemE 75 (B) (1997) 257–265.
[12] E. Croiset, S.F. Rice, R.G. Hanush, Hydrogen peroxide decomposition in supercritical water, AIChE J. 49 (9) (1997) 2343–2352.
[13] APHA, AWWA, WPCF, in: L.S. Clesceri, A.E. Greenberg, R.R. Trussell, (Eds.), Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.
[14] T.D. Thornton, P.E. Savage, Phenol oxidation in supercritical water, J. Supercrit. Fluids 3 (1990) 240–248.
[15] T.D. Thornton, P.E. Savage, Kinetics of phenol oxidation in supercritical water, AIChE J. 32 (3) (1992) 321–327.
[16] T.D. Thornton, P.E. Savage, Phenol oxidation pathways in supercritical water, Ind. Eng. Chem. Res. 31 (11) (1992) 2451–2456.
[17] R. Li, T.D. Thornton, P.E. Savage, Kinetics of CO_2 formation from the oxidation of phenols in supercritical water, Environ. Sci. Technol. 26 (1992) 2388–2395.
[18] V. Tufano, A multi-step kinetic model for phenol oxidation in high pressure water, Chem. Eng. Technol. 16 (1993) 186.
[19] R.K. Helling, J.W. Tester, Oxidation kinetics of carbon monoxide in supercritical water, Energy and Fuels 1 (1987) 417.
[20] C.K. Rofer, G.E. Streit, Kinetics and Mechanisms of Methane Oxidation in Supercritical Water, Los Álamos National Laboratory Report, LA-11439-MS DOE/HWP-64, 1988.
[21] M. Krajnc, J. Levec, On the kinetics of phenol oxidation in supercritical water, AIChE J. 42 (7) (1996) 1977–1984.

[22] S. Gopalan, P.E. Savage, Reaction mechanism for phenol oxidation in supercritical water, J. Phys. Chem. 98 (1994) 646–652.

[23] Y. Oshima, K. Hori, M. Toda, T. Chommanad, Phenol oxidation kinetics in supercritical water, J. Supercrit. Fluids 13 (1998) 241–246.

[24] M. Koo, W.K. Lee, C.H. Lee, New reactor system for supercritical water oxidation and its application on phenol destruction, Chem. Eng. Sci. 52 (7) (1997) 1201–1214.

[25] B.B. Pruden, H. Le, Wet air oxidation of soluble components in waste water, Can. J. Chem. Eng. 54 (1976) 319.

[26] H.R. Devlin, I.J. Harris, Mechanism of the oxidation of aqueous phenol with dissolved oxygen, Ind. Eng. Chem. Fundam. 23 (1984) 387–392.

[27] S. Gopalan, P.E. Savage, Phenol oxidation in supercritical water from global kinetics and product identities to an elementary reaction model, ACS Symp. Ser., 608 (Innovations in Supercritical Fluids) (1995) 217–231.

[28] S. Gopalan, P.E. Savage, A reaction network model for phenol oxidation in supercritical water, AIChE J. 41 (8) (1995) 1864–1873.

[29] J.C. Chang, S.-S. Li, C.-M. Ko, Catalytic wet oxidations of phenol and *p*-chlorophenol contaminated waters, J. Chem. Technol. Biotechnol. 64 (1995) 245–252.

[30] M.T. Harris, R.L. Jolley, G.E. Oswald, J.C. Rose, Wet oxidation of phenol and naphthalene in aqueous and sludge solution: application to coal-conversion wastewater and sludge treatment, Report ORNL/TM-8576 (Oak Ridge National Laboratory), 1983, pp. 1–46.

[31] L. Jaulin, E. Chornet, High shear jet-mixers as two phase reactors: an application to the oxidation of phenol in aqueous media, Can. J. Chem. Eng. 65 (2) (1987) 64–70.

[32] H. Joglekar, S.D. Samant, J.B. Joshi, Kinetics of wet air oxidation of phenol and substituted phenols, Water Res. 25 (2) (1991) 135–145.

[33] A. Sadana, Ph.D. Thesis, University of Delaware, 1976.

[34] L.V. Shibaeva, D.I. Metelitsa, E.T. Denisov, Oxidation of phenol with molecular oxygen in aqueous solutions, Kinet. Catal. 10 (5) (1969) 832–836.

[35] R.S. Willms, A.M. Balinsky, D.D. Reible, D.M. Wetzel, D.P. Harrison, Aqueous-phase oxidation: the intrinsic kinetics of single organic compounds, Ind. Eng. Chem. Res. 26 (1) (1987) 148–154.

[36] V.D. Mundale, H.S. Joglekar, A. Kalam, J.B. Joshi, Regeneration of activated carbon by wet air oxidation, Can. J. Chem. Eng. 69 (1991) 1149–1159.

[37] T.J. Wightman, Studies in supercritical wet air oxidation, M.S. Thesis, Chem. Eng. Dept., MIT, Cambridge, MA, 1981.

[38] R.K. Helling, M.K. Strobel, R.J. Torres, R.L. Jolley, G.E. Ostwald, Kinetics of wet oxidation of biological sludges from coal conversion wastewater treatment, Report OR NL/MIT-332, Oak Ridge National Laboratory, 1981.