36906 PDF

# BY-PRODUCTS FROM SUPERCRITICAL WATER OXIDATION: PATHWAYS, KINETICS, AND MECHANISMS

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## INTRODUCTION

Supercritical water oxidation (SCWO) is an emerging technology for the ultimate destruction of organic wastes. Organic compounds and oxygen can be intimately mixed in a single homogeneous aqueous phase at supercritical conditions ($T_C = 374°C$, $P_C = 218$ atm). Thus, the rapid oxidation reactions are unhindered by inter-phase transport limitations that could occur at subcritical conditions where multiple phases exist. Savage et al. (1) describe current research into SCWO reactions in their review of reactions at supercritical conditions.

The rational design, optimization, control, and analysis of SCWO processes requires a knowledge of SCWO kinetics and potential byproducts formed from the oxidation of real pollutants. Our research group has focused on the oxidation of phenolic compounds (2-10), and this presentation will provide an overview of our most recent work.

## METHODOLOGY

All oxidation experiments were performed in a reactor that nominally operated isothermally, isobarically, and in plug flow. Aqueous solutions of $O_2$ and the phenol were prepared separately and used as the reactor feed streams. The feed streams were pressurized and pumped through the reactor using two liquid chromatography pumps. The phenol and oxygen streams were preheated in separate coils of Hastelloy C-276 tubing. These preheater lines meet in a mixing union, where the temperature was measured by a thermocouple and the mixed feed streams enter the 4 m. long by 0.125 in. O.D. Hastelloy reactor. The preheater lines, mixing tee, and reactor coil are housed in an isothermal fluidized aluminum-oxide bath equipped with a temperature controller.

The reactor effluent was cooled in two consecutive tube-in-tube heat exchangers and decompressed in a back pressure regulator. The exiting stream was separated into gas and liquid phases (at ambient conditions) in a liquid trap. The gas flow rate was measured with a bubble meter at the outlet of the system, and the gas stream was then sent to an on-line gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The liquid flow rate was measured, and samples of the liquid phase were retained for analysis.

A reverse-phase high-performance liquid chromatograph (HPLC) was used to determine the concentration of phenolics in the liquid effluent samples. Analyses were performed isocratically with a mobile phase of water/acetonitrile in a 5:2 v/v ratio flowing at 1 ml/min. The UV absorbance at a wavelength of 210 nm was monitored, and detector response factors were determined experimentally.

Before additional products in the liquid phase were analyzed, the samples were concentrated because many products were present in low concentrations. 20 mL of the reactor effluent was extracted with three successive 10 mL aliquots of dichloromethane. The 30 mL volume of this organic phase was subsequently reduced to 1 mL using a Kuderna-Danish concentrator in a water bath at 50°C. 10 mL of a dichloromethane solution containing a standard was added to each sample prior to concentration.

Reaction products in these concentrated samples were identified by GC-MS. The reaction products were quantified by GC with a flame ionization detector (FID). When a suspected reaction product was available commercially, we positively identified that product by matching both the mass spectrum and retention time with those of the authentic sample. The FID response factor was then determined experimentally for these compounds. Other suspected products, for which the authentic compound was not available commercially, were tentatively identified by inspecting the mass spectra and

matching them to spectra stored in the GC-MS computer database. The response factors for these products were assumed to be equal to those determined experimentally for chemically similar compounds. The GCs were equipped with12 m x 0.2 mm O.D. HP-1 capillary columns. Helium served as the carrier gas, and 1mL of the sample was injected in the splitless mode.

## RESULTS

Thornton et al. (5), Li et al. (3), Martino et al. (10), and Gopalan and Savage (8) identified several multi-ring products (e.g. dibenzofuran, 2 and 4-phenoxyphenol, dibenzo-*p*-dioxin and 2,2'-biphenol) from the oxidation of phenols in supercritical water at temperatures up to 480°C. The formation of dimers is important because some of these are potentially more toxic than the reactant. By determining the concentrations, molar yields, and selectivities of many of these products, we have been able to develop reaction networks that describe the formation of these multi-ring species.

The data of Thornton and Savage (7) for phenol SCWO, and Li et al. (2,3) for SCWO of 2-chlorophenol show some general trends for product selectivities. The dimer selectivity tends to decrease with increasing phenol conversion while the selectivity to gases (CO, $CO_2$) tends to increase with increasing phenol conversion. We developed a reaction network that was consistent with these qualitative trends in the experimental product selectivities. This network considered phenol, dimers, carbon oxides, and "others" as the distinct chemical species. In this network, phenol is consumed by parallel paths that form dimers and "other" products. The dimers decompose to the ring-opening and other products. Finally, the "other" products are oxidized to CO and $CO_2$.

The mathematical modeling of each network involved differential equations for each of the product categories. To determine the rate parameters for each of the four reactions in the model, we employed SimuSolv (11). The parameter estimation process incorporated an integration routine in addition to the optimization. A linear multistep predictor-corrector integration routine, LSODE, was employed in concert with the generalized reduced-gradient method. The entities for which experimental data were obtained; viz. phenol, dimers, and gases, were the response variables. The criterion for parameter estimation was the maximization of the log likelihood function for each of the response variables. The reaction orders $(a_i,b_i)$ for the organic compound and oxygen for each pathway were determined from data at a single temperature, 460°C.

The reaction orders obtained from the regression of data at 460°C were then fixed in the subsequent parameter estimation. Also, the water order for each step was fixed at 0.42, the value obtained for phenol disappearance kinetics. Data at four temperatures; 420, 440, 460 and 480°C were then used to determine the Arrhenius parameters for the four individual reactions. Table 1 displays the results of the parameter estimation process for the network model. The units are kcal, moles, liters, and seconds.

**Table 1. PARAMETERS IN REACTION NETWORK MODEL**

| | Reaction 1 | Reaction 2 | Reaction 3 | Reaction 4 |
|---|---|---|---|---|
| a | 0.89 ± 0.26 | 0.86 ± 1.19 | 0.86 ± 0.30 | 0.50 ± 0.15 |
| b | 0.49 ± 0.23 | 0.48 ± 1.15 | 0.60 ± 0.32 | 1.49 ± 0.31 |
| $E_a$ (kcal/mol) | 10.0 ± 4.7 | 25.5 ± 15.0 | 28.8 ± 4.1 | 44.8 ± 9.0 |
| A ($M^{0.58-a-b}\ s^{-1}$) | $10^{1.8 \pm 1.5}$ | $10^{5.6 \pm 5.5}$ | $10^{8.5 \pm 2.6}$ | $10^{13.5 \pm 2.8}$ |
| k @ 460°C,250 atm | 0.026± 0.009 | .0034 ± 0.0001 | 0.398 ± 0.023 | 0.293 ± 0.054 |

(M = moles of carbon per liter)

We used the model with the parameters in Table 1 to predict the results of phenol SCWO reported by Thornton and Savage (6,7), and Li et al. (2). Figure 1 shows a comparison of the effect of residence time on the phenol conversion and the dimer and gas selectivities at 380°C and 278 atm. The curves, which give the model predictions, capture the trends in the experimental data well.

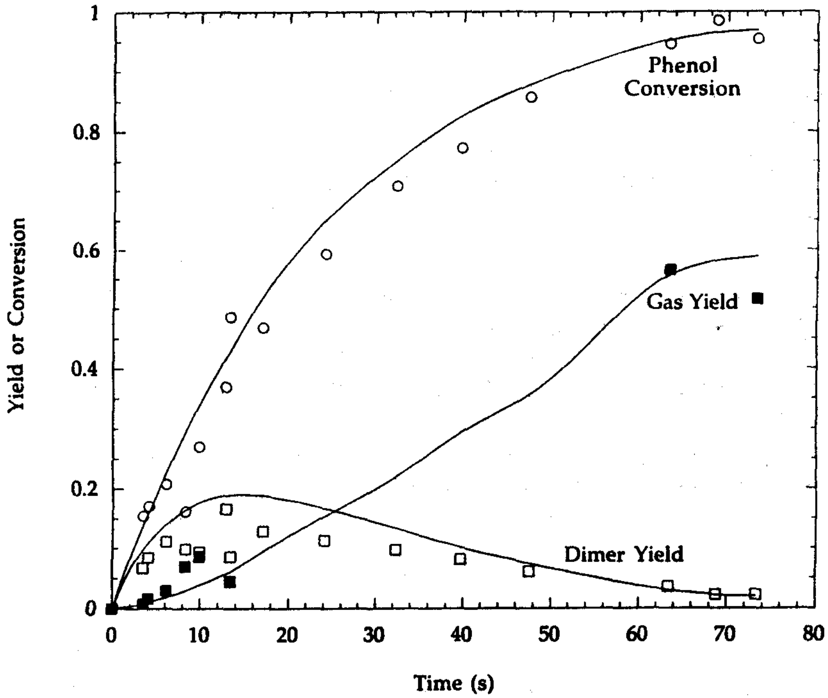

Figure 1. Product Yield vs. Residence Time for Phenol SCWO at 380°C and 278 atm

The estimated activation energies in Table 1 enable us to compare the rate constants for phenol consumption along the competing parallel paths as a function of temperature. The initial dimer selectivities calculated from the model (calculated as $k_1/k_1+k_2$) range from 89% at 420°C to 78% at 480°C. These rate constants when extrapolated to 600°C predict an initial selectivity to dimers of ~45%, which shows that even at higher temperatures dimerization and ring-opening reactions are likely to be equally important. Examining lower temperatures we note that at 380°C, nearly 95% of the initial selectivity of phenol is towards dimers as shown in Figure 1. These results show that dimerization is the main primary pathway for phenol. In fact, at 380°C, the path from phenol to ring-opening and other products is negligible, and the reaction network could be reduced to a set of consecutive reactions.

The model also shows that although the formation of dimers cannot be prevented, the selectivity to dimers decreases with increasing phenol conversion (Figure 1). At complete conversion of phenol the selectivity towards dimers is essentially zero. Also, the destruction of dimers is aided by higher temperatures as is evident from the activation energy for the destruction of dimers (29 kcal/mol) exceeding that for dimer formation (10 kcal/mol). This difference in activation energies translates to an increase in the ratio of the rate constant for destruction of dimers to that for the formation of dimers ($k_3/k_1$) by a factor of 7 when the temperature increases from 380°C to 480°C.

The parameters in Table 1 also show that higher temperatures have the desirable effect of favoring the formation of gases. This is evident from the activation energy for the formation of gases (45 kcal/mol) exceeding the activation energies for the steps leading to the formation of the ring-opening and other intermediates (25 and 29 kcal/mol).

The reaction orders for phenol in Table 1 for the two primary paths are nearly equal, so varying the phenol concentration will have little effect on the product selectivities. The reaction orders for oxygen are also nearly equal for all the steps except for step 4 which has an oxygen order of 1.5. This high oxygen order indicates that high oxygen concentrations will result in higher rates of formation of gases.

In addition to modeling the reactions using empirical reaction networks, we have developed detailed chemical kinetics models based on the reaction mechanisms. This work (9) focuses on adapting gas-phase combustion kinetics to SCWO conditions as the basis for a quantitative model.

## CONCLUSIONS

The products of phenol oxidation in SCW can be categorized as dimers, gases, and ring-opening and other products. The variation of the selectivity of phenol to these products with residence time, temperature and species concentrations can be quantitatively described using a reaction network and the parameters in Table 1. The network includes parallel pathways for phenol to dimers and to ring-opening and other products, secondary decomposition of dimers to ring-opening and other intermediates, and oxidation of these intermediates to carbon oxides.

Dimerization of phenol is the main primary pathway for phenol consumption between 380 and 480°C. A successful strategy for treatment of phenolic wastes by SCWO must ensure the destruction of these dimers and the formation of $CO_2$ in high selectivities. Our quantitative reaction model showed that long residence times and high reaction temperatures favor the destruction of dimers and the formation of CO and $CO_2$. Moreover, the influence of intermediate reaction products (dimers and other products) on the rate of formation of the carbon oxides shows that phenol disappearance kinetics alone constitutes insufficient information for process design. Identifying and quantifying reaction intermediates and developing accurate quantitative reaction models is of vital importance for any rational SCWO process design.

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# OXIDATION AND HYDROLYSIS OF ACETIC ACID AND METHYLENE CHLORIDE IN SUPERCRITICAL WATER AS A MEANS OF REMEDIATION

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## INTRODUCTION

Supercritical water oxidation (SCWO) is a promising technology proposed for the destruction of hazardous organic wastes. Unlike its well known behavior under ambient conditions, water above its critical point (374° C, 221 bar) has properties similar to that of a nonpolar solvent, primarily due to the effect of a decrease in hydrogen bonding and density that occurs near and above the critical point. The result is that nonpolar organics and oxygen exhibit complete solubility in supercritical water, while polar species such as inorganic salts are insoluble and precipitate out. In the single homogeneous phase formed, oxidation of organics with oxygen in supercritical water is rapid and complete to $CO_2$ and $H_2O$. Organic heteroatoms such as halogens, sulfur, or phosphorus are converted to inorganic acids ($HCl$, $H_2SO_4$, $H_3PO_4$) which precipitate as salts when neutralized with added base, while nitrogen is converted to $N_2$ and $N_2O$. No $NO_x$ compounds are formed due to the relatively low temperatures that exist in the SCWO process (400 - 650° C) relative to that of air incineration processes (typically 900 - 1300° C). Oxidation in supercritical water is thus an appealing means of destroying toxic organic compounds while simultaneously separating out undesired inorganics by precipitation. Applications to decontaminating soils and dilute aqueous wastes are of special interest. Earlier work has demonstrated high destruction efficiencies for various organics in SCWO (1).

## METHODOLOGY

Our methodology includes laboratory-scale experiments and interpretive mathematical modeling to deduce global kinetic parameters and a fundamental mechanistic understanding of the destruction pathways of model organic compounds. These model organics are compounds that are either typical and representative wastes and soil contaminants themselves, refractory intermediate compounds formed in the oxidation of a more complex compound, or surrogates for compounds too dangerous to use in the lab (such as chemical weapon agents) but that are chemically similar in some respect to the more toxic compound they represent. Waste destruction efficiencies, yields, and identities of resulting products are measured over ranges of key operating variables (e.g. temperature, pressure, reaction time, organic/oxidant feed ratio, possible presence of solids) pertinent to normal and upset conditions. This paper describes the experimental results of oxidation and hydrolysis (no added oxygen) in supercritical water of two model compounds that have been investigated in our lab - acetic acid and methylene chloride.