12

DOE/PC/92536--T4

QUARTERLY TECHNICAL PROGRESS REPORT

Report for the Quarter: September 1, 1993 - November 30, 1993
DOE Grant Number DE-FG22-92PC92536
Project Title: Oxidation of Phenolics in Supercritical Water
Project Director: Phillip E. Savage
Associate Professor
Chemical Engineering Department
University of Michigan
Ann Arbor, MI 48109-2136

INTRODUCTION

An environmental hazard associated with coal liquefaction and gasification is the generation of aqueous waste streams containing phenolics and carcinogenic organics such as polynuclear aromatics. Oxidation in supercritical water (SCW) is an emerging technology for the ultimate destruction of phenolics and other organics in waste water streams. SCW oxidation involves the oxidation of organics in an aqueous medium at temperatures between 400 - 650°C and pressures around 250 atm. These conditions exceed the thermodynamic critical point of water, hence the water is said to be supercritical. Wastes can be converted by SCWO to benign products: carbon is converted to CO₂, hydrogen to H₂O, and nitrogen to N₂ or N₂O (but not NO_x). SCWO possesses several attractive features.

1) The effluents from the SCWO process can be collected or held in a recycle loop so the process can be easily "bottled up" with no uncontrolled emissions should an upset occur (Modell, 1989; Barner et al., 1992).

2) The oxidation reaction is exothermic, so it is possible to operate the SCWO reactor in an autothermal mode. That is, the oxidation of the organic material in the aqueous stream liberates sufficient heat to maintain the elevated reactor temperature and also preheat the feed. Thus, after start-up, the process would not require an external energy source and could even be used to produce energy provided the organics content in the feed stream was sufficiently high.

3) Operating at supercritical conditions also provides a single, homogeneous fluid phase in the reactor. Indeed, water above its critical point has a high solubility for organics (Connolly, 1966), and it is totally miscible with oxygen (Pray et al., 1952). These solution properties guarantee the presence of a single phase at reaction conditions thereby ensuring intimate contact of the organics and oxygen and the absence of inter-phase transport limitations that can occur in subcritical, wet-air oxidation systems.

4) The temperature in SCWO is high enough to provide rapid reaction rates but not so high that alloys begin to lose their mechanical strength. Thus, the oxidation of organics goes essentially to completion in a very short time (a few seconds). This eliminates the need to treat the reactor off-gases (which are primarily CO₂ and O₂) or liquid effluent (which is clean water).

These factors are among those that make SCWO an attractive alternative to conventional waste destruction schemes.

RESEARCH OBJECTIVES

The objective of this project is to oxidize selected phenolics in SCW and then determine the reaction kinetics (rate constants, reaction orders, activation energies) and the reaction pathways. These reaction fundamentals can then be used to evaluate, design, optimize, and control coal-conversion waste water treatment processes based on SCWO.

Most previous SCWO research has dealt with technology demonstrations (Modell, 1982, 1985, 1989; Thomason and Modell, 1984) and experimental kinetics studies of simple compounds (Helling and Tester, 1987, 1988; Webley and Tester, 1989, 1991). Our continuing work with phenolic compounds (Thornton and Savage, 1990, 1992a,b; Thornton et al., 1991; Li et al., 1992, 1993) is among the small, but growing, body of literature on the SCWO kinetics of actual pollutants in waste water streams (see also Yang and Eckert, 1988).

EXPERIMENTAL

All chemical used in this research are available commercially in high purity. Oxidation reactions are accomplished in an isothermal, high-pressure, flow reactor designed specifically for operation at supercritical water conditions. The reactor feed stream is prepared by mixing two separate streams. One stream is an aqueous solution of the phenolic reactant and the second stream is water with dissolved oxygen. Controlling the flow rates of these two streams allows us to control the reactor residence time and the relative amounts of the phenol and oxygen fed to the reactor. The reactor effluent is cooled and depressurized and then collected for analysis. The gaseous products are analyzed by gas chromatography (GC). The liquid-phase products are analyzed by GC, high-performance liquid chromatography, and GC-mass spectrometry. The experimental details are available in several of our recent publications (e.g., Li et al., 1992, 1993).

RESULTS THIS QUARTER

Our work to date has focused on the oxidation of cresols in SCW. We have explored the effects of temperature, pressure, and the concentrations of o-cresol, oxygen, and water. Table I gives these experimental conditions and the resulting o-cresol conversions. We reported a portion of this data in our previous quarterly report. New information is given in the last three columns where we report the molar yields of phenol, CO₂, and CO. Molar yields were calculated as the molar flow rate of a given product divided by the initial molar flow rate of o-cresol and normalized by the stoichiometric coefficient.

Earlier, we used the o-cresol conversion data to determine the parameters in a global reaction rate law for o-cresol disappearance.

$$rate = A \exp\left(\frac{-E_a}{RT}\right) [o-Cresol]^a [O_2]^b [H_2O]^c$$

Table I: Summary of o-cresol SCWO Experiments.

Temp. (°C)	Pres. (atm)	τ (s)	Concentrations (mol/L)			Conversion (%)	Yield CO (%)	Yield CO2 (%)	Yield Phenol (%)
			o-cresol	oxygen	water				
460.3	251	3.7	1.17E-4	6.64E-3	5.91	56.3%	4.4%	13.8%	13.3%
461.1	250	5.3	1.16E-4	7.10E-3	5.85	76.0%	8.2%	24.3%	23.2%
459.5	250	7.9	1.03E-4	7.44E-3	5.89	83.4%	11.6%	36.8%	24.2%
460.9	250	11.0	1.02E-4	7.37E-3	5.86	96.4%	13.9%	41.9%	29.0%
460.2	250	4.4	1.84E-4	4.87E-3	5.88	47.3%	3.8%	8.3%	10.1%
460.0	251	5.9	1.56E-4	5.44E-3	5.92	67.4%	5.5%	22.1%	20.5%
459.9	251	7.7	1.70E-4	5.09E-3	5.92	76.7%	7.6%	24.5%	22.2%
459.9	250	12.2	1.72E-4	4.91E-3	5.89	94.7%	9.6%	37.2%	27.3%
460.2	250	4.3	2.53E-4	1.08E-2	5.87	34.2%	3.8%	6.9%	9.0%
460.7	250	5.3	2.69E-4	1.01E-2	5.86	34.5%	5.4%	6.8%	9.9%
462.3	251	7.3	2.60E-4	1.03E-2	5.85	52.6%	5.6%	8.2%	12.4%
460.5	250	9.0	3.14E-4	9.30E-3	5.86	58.5%	10.1%	10.1%	14.9%
460.1	250	5.5	3.64E-4	9.22E-3	5.87	41.9%	4.3%	6.2%	8.6%
459.9	250	5.4	4.37E-4	7.80E-3	5.88	40.9%	3.9%	6.5%	8.3%
460.0	250	7.7	4.19E-4	8.09E-3	5.88	55.1%	6.5%	11.5%	11.2%
460.0	250	12.0	4.59E-4	7.44E-3	5.88	72.1%	9.2%	16.0%	14.7%
460.1	250	5.5	4.42E-5	2.46E-3	5.89	67.9%	5.9%	20.9%	24.1%
460.4	252	7.7	4.43E-5	2.49E-3	5.95	83.4%	6.6%	22.4%	25.4%
460.0	251	12.6	4.53E-5	2.41E-3	5.93	97.6%	10.1%	34.2%	34.1%
460.3	250	4.4	2.35E-5	1.19E-3	5.89	61.0%	2.7%	13.9%	23.3%
459.9	250	5.4	2.31E-5	1.21E-3	5.90	63.6%	3.6%	14.5%	21.7%
459.8	251	12.9	2.20E-5	1.27E-3	5.93	88.1%	6.3%	29.6%	50.7%
350.0	250	29.5	5.88E-4	4.26E-2	34.73	98.4%	6.6%	42.7%	0.1%
370.0	250	25.1	5.43E-4	3.66E-2	30.11	98.0%	6.6%	37.5%	1.7%
380.2	250	15.6	4.13E-4	3.14E-2	25.19	72.7%	3.1%	20.1%	4.4%
380.9	250	20.7	4.12E-4	2.90E-2	24.31	78.1%	3.8%	21.0%	3.3%
379.6	250	46.3	4.16E-4	3.24E-2	25.95	99.5%	9.6%	52.8%	0.6%
400.2	250	8.0	1.73E-4	1.16E-2	9.61	30.4%	0.5%	3.8%	2.5%
420.4	250	4.6	1.23E-4	9.25E-3	7.49	18.7%	0.6%	5.2%	4.0%
420.6	251	6.3	1.28E-4	9.13E-3	7.54	29.6%	1.1%	9.7%	4.1%
420.5	250	13.2	1.20E-4	9.28E-3	7.48	51.7%	2.8%	15.5%	11.1%
440.3	250	5.5	1.17E-4	7.82E-3	6.51	44.0%	1.8%	9.3%	10.0%
480.9	250	4.5	9.26E-5	6.55E-3	5.41	85.0%	9.3%	31.3%	30.3%
499.7	250	4.3	8.68E-5	6.15E-3	5.07	98.3%	12.5%	50.7%	32.7%
460.1	200	3.6	8.17E-5	5.20E-3	4.29	40.5%	3.3%	12.5%	16.9%
460.2	220	4.1	7.91E-5	5.92E-3	4.88	42.5%	4.6%	14.7%	16.1%
460.2	230	4.4	9.91E-5	6.31E-3	5.20	44.3%	4.4%	14.5%	15.9%
460.3	240	4.7	8.96E-5	6.73E-3	5.53	41.0%	7.7%	8.5%	12.1%
460.0	260	5.3	1.01E-4	7.59E-3	6.25	52.3%	9.7%	14.5%	14.5%
459.8	270	5.7	1.26E-4	8.05E-3	6.63	64.5%	7.4%	52.9%	18.2%
460.1	280	6.0	1.13E-4	8.51E-3	7.00	62.5%	10.6%	20.1%	16.3%
459.5	300	6.9	1.51E-4	9.61E-3	7.91	77.0%	13.9%	30.2%	16.9%

The rate law parameters were determined using a non-linear regression routine in SYSTAT, a statistical software package. To accomplish this parameter estimation we combined the global rate law expression with the design equation for the plug-flow reactor used in the experiments to obtain

$$\left[(1-X)^{1-a} - 1 \right] = (a-1)A \exp\left(\frac{-E_a}{RT}\right) [o-Cresol]^{a-1} [O_2]^b [H_2O]^c \tau$$

The procedure for deriving the previous equation was presented in one of our recent publications (Li et al., 1993). The results of the present analysis led to the estimates for the parameters shown in the rate law below for o-cresol disappearance. These parameters differ slightly from those in the preliminary rate law we gave in the previous quarter's report.

$$\text{Rate of Cresol disappearance} = 10^{5.6} \exp\left(\frac{-29,100}{RT}\right) [\text{o-cresol}]^{0.57} [\text{O}_2]^{0.25} [\text{H}_2\text{O}]^{1.40}$$

The ability of the rate law to correlate the experimental data can be assessed by inspecting Figure 1, which is a parity plot that give the calculated conversion of o-cresol as a function of the conversion calculated from the rate law. A perfect correlation would result in all of the data falling on the diagonal line in the plots. Clearly, the correlation is not perfect, but it does give a good representation of the experimental data. No systematic deviations from the correlation are evident.

Figure 1: Parity plot for o-cresol Conversion.

We have extended our kinetics analysis for o-cresol to determine the global rate law for the conversion of total organic carbon (TOC) into CO₂. This rate law is important from an environmental perspective because it gives the kinetics for the destruction of organic carbon, which is the goal of SCWO technology.

$$\text{Rate of CO}_2 \text{ Production} = 10^{7.1} \exp\left(\frac{-35,000}{RT}\right) [\text{TOC}]^{0.41} [\text{O}_2]^{0.65} [\text{H}_2\text{O}]^{1.27}$$

The rate of CO₂ production depends more strongly on the oxygen concentration and less strongly on the organic concentration than does the rate of cresol disappearance. This observation is consistent with our work with phenol and 2-chlorophenol oxidation in SCW.

In both rate laws, the concentrations are in mol/L, time is in seconds, and *E_a* has units of cal/mol.

The ability of this rate law to correlate the experimental data can be assessed by inspecting Figure 2. Again, the correlation is not perfect, but it gives a good representation of the experimental data. No systematic deviations from the correlation are evident.

Figure 2: Parity plot for Organic Carbon Destruction

Figure 3 relates the conversion of organic carbon to CO₂ (*X_c*) with the o-cresol conversion (*X*). It is clear that the o-cresol conversion always exceeds the organic carbon conversion. This observation indicates that products other than CO₂ are formed as o-cresol disappears.

Figure 3: Carbon dioxide yield versus o-cresol conversion.

Indeed, our analyses of the products from SCWO of o-cresol have shown that there are a large number of reaction products. The major product appears to be phenol. The phenol yields were quantified using HPLC, and Table 1 gives the yields obtained in each of the experiments. We desired to determine whether phenol was a primary product (i.e., formed directly from the o-cresol). The Delplot methodology (Bhore et al., 1990) provides a convenient means for ascertaining the order of appearance of reaction products. The method, in its simplest form, requires plots of the product's selectivity (yield/conversion) as a function of conversion. Products with non-zero initial selectivities are, by definition, primary products, whereas products with initial selectivities equal to zero are formed later in the reaction network. Figure 4 gives the Delplot for phenol at one set of reaction conditions (460°C, 250 atm, initial cresol concentration = 0.0004 mol/L, and initial oxygen concentration = 0.008 mol/L). It is clear that the initial selectivity is non-zero (about 0.21). Therefore, phenol is a primary product, and the reaction network for o-cresol conversion must include a step for o-cresol conversion to phenol. Obtaining quantitative data for other reaction products and performing this Delplot analysis will enable us to build up the entire reaction network.

To gain additional insight into the identities of the other organic compounds formed during o-cresol oxidation, we have extracted the organics in the reactor effluent into methylene chloride and then analyzed the extracts using a GC-MS. A representative total ion chromatogram appears in Figure 5. The numbers appearing near the different peaks correspond to the numbered compounds in Figure 6. Some of these identifications remain tentative. The reaction conditions were $T = 460^\circ\text{C}$, $P = 250\text{ atm}$, $\tau = 12\text{ s}$, $[\text{cresol}] = 0.00046\text{ M}$, and $[\text{O}_2] = 0.0074\text{ M}$.

Figure 4: Phenol Delplot.

Figure 5: Total Ion Chromatogram of o-cresol SCWO reaction effluent.

Clearly, the number of individual compounds is large. We plan to analyze additional samples and obtain quantitative information for as many products as possible.

Figure 6: Index of compounds detected by GC-MS.

One final area of activity during this last quarter has been our initiating experiments to explore the effects of structure on the reactivity of phenolic compounds. The experiments have been performed only recently, and they have not yet been replicated. As such, they should be taken as preliminary results. Table 2 gives the results for the oxidation of the three cresol isomers at identical reaction conditions. p-Cresol is much more reactive than the other two isomers, which indicates that the structure (location of methyl substituent) does influence the reactivity. We plan to oxidize a number of different compounds to obtain rate constants that can be used in quantitative structure-reactivity relations.

Table 2: *Effect of substituent position on the SCWO of cresols at $T = 460\text{ }^{\circ}\text{C}$, $P = 250\text{ atm}$, $\tau = 1.3\text{ s}$, $[\text{cresol}] = 400$, Excess $\text{O}_2 = 150\%$.*

Compound	% Conversion
o-cresol	0.1%
m-cresol	0.1%
p-cresol	14.3%

PLANS FOR THE NEXT QUARTER

Our plans for the next quarter are to obtain more quantitative data for the concentrations of several of the different byproducts formed during the oxidation of o-cresol and then use this information to develop a set of reaction pathways for o-cresol oxidation. Our primary focus, however, will be on developing quantitative structure-reactivity correlations for SCW oxidation of phenolics. We will explore the use of the Hammett relation as the basis for our correlations. We will also conduct experiments with additional compounds to obtain the reactivity data needed to establish the correlation

LITERATURE CITED

- Barner, H. E., Huang, C. Y., Johnson, T., Jacobs, G., Martch, M. A., Killilea, W. R., *J. Haz. Mat.*, **1992**, 31, 1.
- Bhore, N. A., Klein, M. T., Bischoff, K. B., *Ind. Eng. Chem. Res.* **1990**, 29, 313.
- Connolly, J. F. *Chem. Eng. Data*, **1966**, 11, 13.
- Helling, R. K., Tester, J. W. *Energy and Fuels*, **1987**, 1, 417.
- Helling, R. K., Tester, J. W. *Env. Sci. Tech.*, **1988**, 22, 1319.
- Li, R., Szmukler, D., Savage, P. E. *AIChE J.* **1993**, 39, 178.
- Li, R., Thornton, T. D., Savage, P. E. *Env. Sci. Technol.* **1992**, 26, 2388.

- Modell, M. U. S. Patent No. 4,338,199 **1982**.
- Modell, M. U. S. Patent No. 4,543,190 , **1985**.
- Modell, M. *Standard Handbook of Hazardous Waste Treatment and Disposal*, H. M. Freeman, Ed., **1989**, McGraw-Hill, Section 8.11
- Pray, H. A., Schweickert, C. E., Minnich, B. H. *Ind. Eng. Chem.* **1952**, 44, 1146.
- Thomason, T. B., Modell, M., *Hazard. Waste*, **1984**, 1, 453.
- Thornton, T. D., Savage, P. E., *J. Supercritical Fluids*, **1990**, 3, 240.
- Thornton, T. D., LaDue, D. E., Savage, P. E., *Env. Sci. Tech.*, **1991**, 25, 1507.
- Thornton, T. D., Savage, P. E., *AIChE J*, **1992a**, 38, 321.
- Thornton, T. D., Savage, P. E., *Ind. Eng. Chem. Res.*, **1992b**, 31, 2451.
- Webley, P. A., Tester, J. W., *Energy and Fuels*, **1991**, 5, 411.
- Webley, P. A., Tester, J. W., *ACS Symp. Series No. 406*, **1989**, 259.
- Yang, H. H., Eckert, C. A. *Ind. Eng. Chem. Research*, **1988**, 27, 2009.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DATE

FILMED

4 / 12 / 94

END