QUARTERLY TECHNICAL PROGRESS REPORT

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Project Title:	Oxidation of Phenolics in Supercritical Water
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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 SCW oxidation.

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 SCW oxidation 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 o-cresol in SCW. We have explored the effects of temperature, pressure, and the concentrations of cresol, oxygen, and water. The table on the next page gives these experimental conditions and the resulting o-cresol conversions. We used these data to determine the parameters in a global reaction rate law for o-cresol disappearance.

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

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

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

Summary of o-cresol Experiments

Temp. (°C)	Pres. (atm)	τ (s)	Concentrations (mol/L)			Conversion (%)
			o-cresol	oxygen	water	
461.2	249	9.151	2.669E-4	0.000E+0	5.828E+0	1.36%
461.2	250	17.730	2.685E-4	0.000E+0	5.864E+0	9.77%
461.2	249	43.304	2.669E-4	0.000E+0	5.828E+0	3.12%
460.3	251	3.735	1.165E-4	6.643E-3	5.911E+0	56.26%
461.1	250	5.339	1.164E-4	7.099E-3	5.854E+0	76.00%
459.5	250	7.934	1.031E-4	7.442E-3	5.895E+0	83.39%
460.9	250	10.992	1.021E-4	7.367E-3	5.859E+0	96.37%
460.2	250	4.448	1.838E-4	4.871E-3	5.881E+0	47.26%
460.0	251	5.946	1.560E-4	5.441E-3	5.921E+0	67.39%
459.9	251	7.679	1.701E-4	5.086E-3	5.924E+0	76.68%
459.9	250	12.200	1.720E-4	4.913E-3	5.888E+0	94.66%
460.2	250	4.321	2.526E-4	1.082E-2	5.870E+0	34.23%
460.7	250	5.290	2.686E-4	1.007E-2	5.858E+0	34.47%
462.3	251	7.332	2.599E-4	1.035E-2	5.852E+0	52.64%
460.5	250	8.974	3.140E-4	9.298E-3	5.865E+0	58.49%
460.1	250	5.519	3.637E-4	9.221E-3	5.875E+0	41.88%
459.9	250	5.418	4.373E-4	7.801E-3	5.882E+0	40.90%
460.0	250	7.720	4.190E-4	8.088E-3	5.879E+0	55.08%
460.0	250	11.952	4.590E-4	7.437E-3	5.880E+0	72.09%
460.1	250	5.536	4.415E-5	2.457E-3	5.889E+0	67.91%
460.4	252	7.739	4.432E-5	2.486E-3	5.952E+0	83.36%
460.0	251	12.599	4.531E-5	2.412E-3	5.927E+0	97.63%
460.3	250	4.350	2.347E-5	1.190E-3	5.886E+0	60.99%
459.9	250	5.379	2.309E-5	1.211E-3	5.896E+0	63.61%
459.8	251	12.902	2.196E-5	1.267E-3	5.934E+0	88.07%
350.0	250	29.509	5.878E-4	4.260E-2	3.473E+1	98.40%
370.0	250	25.059	5.433E-4	3.657E-2	3.011E+1	97.98%
380.2	250	15.635	4.126E-4	3.135E-2	2.519E+1	72.73%
380.9	250	20.714	4.115E-4	2.902E-2	2.431E+1	78.15%
379.6	250	46.307	4.157E-4	3.244E-2	2.595E+1	99.53%
400.2	250	8.017	1.735E-4	1.160E-2	9.612E+0	30.40%
420.4	250	4.626	1.226E-4	9.247E-3	7.485E+0	18.73%
420.6	251	6.278	1.275E-4	9.128E-3	7.535E+0	29.57%
420.5	250	13.232	1.198E-4	9.284E-3	7.479E+0	51.65%
440.3	250	5.458	1.174E-4	7.818E-3	6.505E+0	44.01%
480.9	250	4.541	9.256E-5	6.548E-3	5.406E+0	84.96%
499.7	250	4.308	8.683E-5	6.146E-3	5.072E+0	98.25%
460.1	200	3.551	8.166E-5	5.197E-3	4.286E+0	40.54%
460.2	220	4.060	7.909E-5	5.917E-3	4.882E+0	42.53%
460.2	230	4.357	9.908E-5	6.308E-3	5.200E+0	44.32%
460.3	240	4.679	8.957E-5	6.732E-3	5.529E+0	41.01%
460.0	260	5.323	1.012E-4	7.590E-3	6.245E+0	52.29%
459.8	270	5.689	1.264E-4	8.055E-3	6.632E+0	64.47%
460.1	280	5.985	1.134E-4	8.507E-3	7.003E+0	62.49%
459.5	300	6.896	1.507E-4	9.610E-3	7.907E+0	76.98%

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 preliminary estimates for the parameters shown in the rate law below for o-cresol disappearance.

$$rate = 10^{5.9} \exp\left(\frac{-15400}{T(K)}\right) [o-Cresol]^{0.67} [O_2]^{0.09} [H_2O]^{1.6}$$

Additional work will allow us to confirm these parameter estimates and determine the 95% confidence intervals for each.

PLANS FOR THE NEXT QUARTER

Our plans for the next quarter are to complete the analysis of the data obtained from the o-cresol oxidation experiments. Specifically, we will determine the parameters in a global rate law for the conversion of total organic carbon (TOC) to CO₂ during o-cresol oxidation. We have already reported the methodology for performing this analysis (Li et al., 1992). We will also obtain quantitative data for the concentrations of several of the different byproducts formed during the oxidation and then use this information to develop a set of reaction pathways for o-cresol oxidation. Finally, we will continue to explore the possibility of developing quantitative structure-reactivity correlations for SCW oxidation of phenolics. We currently have data for the oxidation of phenol, 2-chlorophenol, 2-nitrophenol, and 2-methylphenol. We will likely oxidize other substituted phenols prior to developing the structure-reactivity relationships.

Other plans worthy of noting here are that the graduate student working on this project as his Ph.D. research will be writing and defending his research proposal during the next quarter. This process is the final hurdle a student must clear to qualify for the Ph.D. program. We are also pleased to report that we will be presenting a paper at the AIChE National meeting in Atlanta in April 1994. The paper will describe our current work being supported by this grant.

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