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QUARTERLY TECHNICAL PROGRESS REPORT

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DOE Grant Number DE-FG22-92PC92536
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 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; Crain et al., 1993).

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).

PREVIOUS RESULTS

Our previous work on this project has focused on the oxidation of o-cresol 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 and CO, CO₂, and phenol yields. 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.

We used the o-cresol conversion data to determine the parameters in a global reaction rate law, with the form given below, for o-cresol disappearance.

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

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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 this analysis led to the estimates for the parameters shown in the rate law below for o-cresol disappearance.

$$\text{Rate of Cresol disappearance} = 10^{5.6} \exp\left(\frac{-29,100}{RT}\right) [o\text{-cresol}]^{0.57} [O_2]^{0.25} [H_2O]^{1.40}$$

The ability of the rate law to correlate the experimental data can be assessed by inspecting Figure 1, which is a parity plot that gives 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 also determined 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.

$$\text{Rate of CO}_2 \text{ Production} = 10^{7.1} \exp\left(\frac{-35,000}{RT}\right) [TOC]^{0.41} [O_2]^{0.65} [H_2O]^{1.27}$$

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 (Li et al., 1992, 1993). 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 CO_2 (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 CO_2 are formed as o-cresol disappears. 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 3: Carbon dioxide yield versus o-cresol conversion.

Figure 4: Phenol Delplot.

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 $T = 460\text{ }^{\circ}\text{C}$, $P = 250\text{ atm}$, $\tau = 12\text{ s.}$, $[\text{cresol}] = 0.00046\text{ M}$, and $[\text{O}_2] = 0.0074\text{ M}$.

Figure 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. Work in this area was one of our main activities during this 7th quarter.

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

We have also conducted experiments and obtained data for the oxidation of other phenolics. This information can be used to develop structure-reactivity relationships for the oxidation of phenolics in SCW. We have completed experiments with m- and p-cresol. Tables 2 and 3 list the experimental results.

Table 2: Summary of m-cresol SCWO Experiments.

Temp. (°C)	Pres. (atm)	τ (s)	Concentrations (mol/L)			Conversion (%)	Yield CO (%)	Yield CO ₂ (%)
			m-cresol	oxygen	water			
460.0	250	1.3	3.96E-4	8.54E-3	5.88	0.1%		
460.1	250	3.5	3.56E-4	9.03E-3	5.87	11.3%	1.3%	2.4%
459.8	250	5.1	3.43E-4	8.95E-3	5.88	12.6%		
459.9	250	7.5	3.03E-4	9.73E-3	5.88	18.1%	2.7%	7.8%
460.1	250	10.2	3.11E-4	9.29E-3	5.87	34.9%	3.4%	10.0%
460.2	250	7.4	5.95E-5	3.80E-3	5.88	23.8%	1.8%	12.4%
460.0	250	7.5	1.72E-4	3.83E-3	5.89	20.8%	1.1%	3.6%
460.4	250	5.0	3.84E-5	5.03E-3	5.88	20.3%	3.6%	10.4%
460.4	250	5.1	1.06E-4	5.16E-3	5.88	10.7%	2.2%	3.8%
459.7	250	7.5	6.96E-5	7.14E-3	5.89	34.3%	4.8%	11.6%
460.7	250	7.4	2.70E-4	7.04E-3	5.86	24.1%	1.9%	4.9%
460.3	250	5.0	4.60E-5	9.38E-3	5.87	29.4%	6.2%	14.3%
459.6	250	5.0	1.80E-4	9.35E-3	5.89	23.7%	2.8%	5.2%

Table 3: Summary of p-cresol SCWO Experiments.

Temp. (°C)	Pres. (atm)	τ (s)	Concentrations (mol/L)			Conversion (%)	Yield CO (%)	Yield CO ₂ (%)
			p-cresol	oxygen	water			
460.0	250	1.3	3.96E-4	8.54E-3	5.88	14.3%		
459.9	250	3.5	3.51E-4	9.42E-3	5.88	21.7%		
459.9	250	5.5	3.59E-4	8.72E-3	5.88	18.0%	1.6%	2.8%
460.0	251	7.3	3.14E-4	9.94E-3	5.91	41.9%	1.4%	
460.3	250	10.5	2.93E-4	9.43E-3	5.87	43.9%	2.8%	7.1%
460.3	250	7.4	6.30E-5	3.91E-3	5.88	38.2%	2.3%	5.3%
460.1	250	7.4	1.57E-4	3.92E-3	5.89	32.4%	1.3%	4.1%
460.4	250	4.9	4.26E-5	5.07E-3	5.88	40.4%	2.3%	11.9%
460.0	250	4.9	1.07E-4	5.07E-3	5.89	29.5%		
460.1	250	7.3	5.22E-5	7.02E-3	5.88	58.2%	4.4%	13.6%
460.0	250	7.4	1.54E-4	7.10E-3	5.88	42.8%		
460.1	250	4.9	3.34E-5	9.27E-3	5.88	51.0%	4.8%	10.2%
459.9	250	4.9	1.03E-4	9.19E-3	5.88	42.3%	3.3%	4.4%

The data in Tables 2 and 3 were used in SYSTAT to develop global rate laws for the oxidation of these compounds at 460°C and 250 atm. The rate laws are

$$\text{Rate of } m\text{-Cresol disappearance} = 0.039[m\text{-cresol}]^{0.67}[O_2]^{0.59}$$

$$\text{Rate of } p\text{-Cresol disappearance} = 0.029[p\text{-cresol}]^{0.61}[O_2]^{0.53}$$

RESULTS THIS QUARTER

We have continued to conduct experiments with phenolic compounds. During this quarter we obtained data for the oxidation of p-nitrophenol in SCW. Although nitrophenols are probably not important components in coal-conversion wastewaters, they are useful in our quest to develop structure-reactivity relations for SCWO of phenolics.

Table 4 gives the experimental data for the six p-nitrophenol oxidation runs we have completed to date.

Table 4: Experimental Data for SCWO of p-Nitrophenol

Temp. (°C)	Pres. (atm)	τ (s)	Concentrations (mol/L)			Conversion (%)	Yield Phenol (%)
			p-nitrophenol	oxygen	water		
460.2	250	1.004	9.64E-5	5.03E-3	5.88	21.1%	6.2%
460.1	250	1.198	8.61E-5	5.97E-3	5.88	23.6%	7.2%
460.3	250	0.676	1.84E-4	7.12E-3	5.87	28.6%	3.9%
460.8	250	0.941	1.79E-4	7.30E-3	5.86	38.9%	4.2%
459.9	250	2.012	4.27E-5	9.90E-3	5.88	55.0%	16.5%
460.3	250	2.015	1.83E-4	9.90E-3	5.87	67.1%	19.1%

We used these data to obtain a global reaction rate law for p-nitrophenol oxidation at 460°C. This rate law is

$$\text{Rate of } p\text{-Nitrophenol disappearance} = 15900[p\text{-nitrophenol}]^{1.40}[O_2]^{1.39}$$

We emphasize that this rate law is tentative because of the small amount of data used to determine its parameters.

Using this rate law and rate laws determined previously for o-, m-, and p-cresol and phenol and o-chlorophenol oxidation at 460°C, we can compare the reactivity of these different substituted phenols by comparing reaction rates (or pseudo-first-order rate constants) at identical reaction conditions. Table 5 summarizes the results of this comparison, where the organic concentration was 10^{-4} mol/liter and the oxygen concentration was 7×10^{-3} mol/liter.

Table 5: Comparison of Pseudo-First-Order Kinetics for SCWO of Phenolics

Compound	k (s ⁻¹)
phenol	0.033
o-chlorophenol	0.038
m-cresol	0.044
p-cresol	0.075
o-cresol	0.150
p-nitrophenol	0.404

The data in Table 5 clearly show that structure (e.g., presence of a substituent and its location) influences reactivity for SCWO. The presence of the methyl substituent in the cresols leads to faster kinetics in all three cases, but the ortho isomer is affected the most. Significantly, the reaction pathways for the ortho isomer appear to differ from the meta- and para isomers. o-Cresol oxidation led to high yields of phenol, as shown in Table 1, but m- and p-cresol oxidation did not lead to appreciable phenol yields. Thus, the enhanced reactivity of the o-cresol isomer may simply be a reflection of a rapid demethylation to form phenol, which would then oxidize more slowly. p-Nitrophenol, which also exhibited an enhanced reactivity, likewise showed a high selectivity to phenol formation.

With the data in Table 5, we have begun to develop structure-reactivity relations for SCWO. Our first attempt at finding such a relationship employed the Hammett relation. This relation had been used extensively to correlate structure and reactivity for a large number of different reactions involving substituted aromatics. The relation consists of a semilog plot of the rate constant or reaction rate against Hammett substituent parameters. The correlation has the form

$$\log \frac{k_i}{k_o} = \rho \sigma_i$$

where σ is the Hammett substituent parameter for a specific group (e.g., methyl, nitro, etc.) at a specific aromatic location (o-, m-, p-). These substituent parameters are available in the literature. Figure 7 shows the Hammett plot for our SCWO data for phenolics. We have omitted the data for ortho-substituted phenolics because the Hammett relation typically fails for ortho substituents.

Figure 7: Hammett Plot for SCWO of Phenolics

Figure 7 shows that a linear trend is apparent in the limited data we have obtained to date. As we conduct experiments with additional compounds we will be able to better determine the adequacy of the Hammett relation.

Other work this quarter focused on quantifying the yields of byproducts formed during the oxidation of o-cresol. Table 6 gives the yields of several of these

Table 6: Product Yields for SCWO of o-Cresol

Temp. (°C)	Pres. (atm)	τ (s)	Concentrations (mol/L)			Product concentrations (ppm)						
			o-cresol	oxygen	water	Phenol	SAL	p-cresol	2-HAP	IND	FLU	XAN
461.1	250	5.3	1.16E-4	7.10E-3	5.85	33.37	29.73	0.31	0.23	4.08	0.01	0.00
460.9	250	11.0	1.02E-4	7.37E-3	5.86	26.54	5.19	0.10	0.16	2.78	0.00	0.00
459.5	250	7.9	1.03E-4	7.44E-3	5.89	23.48	12.19	0.15	0.15	3.09	0.28	0.00
460.2	250	4.4	1.84E-4	4.87E-3	5.88	26.48	61.36	0.72	0.20	4.31	0.00	0.00
460.3	251	3.7	1.17E-4	6.64E-3	5.91	16.54	30.25	0.31	0.10	2.24	0.00	0.00
459.9	251	7.7	1.70E-4	5.09E-3	5.92	48.99	45.37	0.44	0.43	5.67	0.00	0.67
460.0	251	5.9	1.56E-4	5.44E-3	5.92	27.58	30.65	0.29	0.21	3.32	0.09	0.55
459.9	250	12.2	1.72E-4	4.91E-3	5.89	66.97	11.82	0.19	0.38	3.25	0.29	1.15
462.3	251	7.3	2.60E-4	1.03E-2	5.85	39.56	76.52	1.09	0.17	7.94	0.36	0.00
460.5	250	9.0	3.14E-4	9.30E-3	5.86	40.69	69.30	0.98	0.32	15.00	0.00	0.62
460.7	250	5.3	2.69E-4	1.01E-2	5.86	25.83	85.77	1.21	0.20	9.53	0.33	0.00
460.1	250	5.5	3.64E-4	9.22E-3	5.87	45.64	106.13	1.27	0.30	10.48	0.00	0.00
460.2	250	4.3	2.53E-4	1.08E-2	5.87	9.07	30.69	0.75	0.18	4.47	0.04	0.00
459.9	250	5.4	4.37E-4	7.80E-3	5.88	20.29	51.90	1.01	0.39	11.57	0.10	0.58
460.0	250	12.0	4.59E-4	7.44E-3	5.88	33.80	43.03	0.46	0.66	14.36	0.08	1.73
460.0	250	7.7	4.19E-4	8.09E-3	5.88	29.72	66.21	0.86	0.57	7.12	1.10	0.59
460.1	250	5.5	4.42E-5	2.46E-3	5.89	6.62	6.22	0.06	0.05	0.49	0.29	0.24
460.0	251	12.6	4.53E-5	2.41E-3	5.93	11.70	1.17	0.00	0.00	0.96	0.00	0.00
460.4	252	7.7	4.43E-5	2.49E-3	5.95	8.00	3.04	0.00	0.05	0.47	0.00	0.00
459.9	250	5.4	2.31E-5	1.21E-3	5.90	3.76	3.75	0.00	0.00	0.11	0.00	0.00
459.8	251	12.9	2.20E-5	1.27E-3	5.93	11.83	1.45	0.00	0.00	0.28	0.00	0.00
460.3	250	4.4	2.35E-5	1.19E-3	5.89	4.50	4.59	0.00	0.00	0.27	0.00	0.00
370.0	250	25.1	5.43E-4	3.66E-2	30.11	0.74	1.42	0.00	0.00	0.00	0.00	0.00
400.2	250	8.0	1.73E-4	1.16E-2	9.61	2.14	11.56	0.37	0.00	0.47	0.29	0.00
440.3	250	5.5	1.17E-4	7.82E-3	6.51	10.00	24.58	0.25	0.05	1.38	0.16	0.00
350.0	250	29.5	5.88E-4	4.26E-2	34.73	0.21	0.72	0.00	0.10	0.00	0.05	0.00
380.9	250	20.7	4.12E-4	2.90E-2	24.31	3.22	6.91	0.13	0.07	0.14	0.15	0.00
420.6	251	6.3	1.28E-4	9.13E-3	7.54	3.92	16.35	0.25	0.00	0.24	0.25	0.00
480.9	250	4.5	9.26E-5	6.55E-3	5.41	30.77	8.96	0.00	0.12	1.56	0.22	0.00
499.7	250	4.3	8.68E-5	6.15E-3	5.07	27.85	1.08	0.00	0.08	0.68	0.00	0.00
380.2	250	15.6	4.13E-4	3.14E-2	25.19	2.84	6.78	0.17	0.00	0.16	0.20	0.00
420.4	250	4.6	1.23E-4	9.25E-3	7.49	4.72	23.12	0.47	0.00	0.41	0.43	0.00
420.5	250	13.2	1.20E-4	9.28E-3	7.48	5.01	8.70	0.10	0.03	0.66	0.00	0.00
379.6	250	46.3	4.16E-4	3.24E-2	25.95	0.17	0.13	0.00	0.05	0.17	0.36	0.00
460.3	240	4.7	8.96E-5	6.73E-3	5.53	10.86	22.58	0.23	0.05	2.19	0.34	0.00
460.0	260	5.3	1.01E-4	7.59E-3	6.25	12.25	20.69	0.20	0.07	2.74	0.00	0.00
460.1	280	6.0	1.13E-4	8.51E-3	7.00	18.82	22.46	0.22	0.10	3.83	0.00	0.00
460.2	220	4.1	7.91E-5	5.92E-3	4.88	22.18	39.13	0.31	0.00	2.38	0.00	0.00
460.2	230	4.4	9.91E-5	6.31E-3	5.20	19.30	31.68	0.30	0.10	2.40	0.00	0.00
460.1	200	3.6	8.17E-5	5.20E-3	4.29	19.84	33.06	0.27	0.00	1.40	0.00	0.00
459.5	300	6.9	1.51E-4	9.61E-3	7.91	20.65	18.78	0.19	0.17	4.85	0.00	0.00
459.8	270	5.7	1.26E-4	8.05E-3	6.63	8.32	10.12	0.10	0.06	1.54	0.00	0.51

reaction products. Partial oxidation products include phenol, salicaldehyde (SAL), p-cresol, 2-hydroxyacetophenone (2-HAP), 1-indanone (IND), 9-fluorenone (FLU), and 9-xanthone (XAN). We will use these data to examine the reaction pathways.

PLANS FOR THE NEXT QUARTER

Our plans for the next quarter are primarily to continue working toward quantitative structure-reactivity correlations for SCWO of phenolics. We will conduct experiments with additional compounds to obtain the reactivity data needed to establish the correlation. We will also explore the ability of other reactivity indices to correlate our experimental results. A secondary focus, however, will continue to be on the quantitative analysis of the different byproducts formed during the oxidation of cresols, nitrophenols, and other phenolics. We will then use this information to develop a set of reaction pathways.

We are currently preparing a paper that describes the results of the research that has been supported by this DOE grant. This paper will focus on o-cresol oxidation in SCW, and we plan to submit it to *Ind. Eng. Chem. Res.* during the next quarter. This will mark the first refereed publication arising from this DOE project.

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10 / 5 / 94

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