

# A Kinetic Study of the SCWO of a Sulfonated Lignin Waste Stream

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The kinetics of the supercritical water oxidation (SCWO) of a sulfonated lignin waste from an industrial source was investigated using a semi-batch, continuous-flow tube reactor. Experiments were carried out at reduced pressures from 0.9 to 1.4 and reduced temperatures from 0.9 to 1.2. In addition, the feed concentration, excess oxidant, flow rate in the reactor, and reactor length were varied to obtain a wide range of experimental residence times and conversions. The residence time and conversion data were used to calculate the reaction orders and Arrhenius parameters. The kinetic model was validated by comparison of the predicted to the experimental conversions. Overall, the results of the kinetic analysis were found to compare very favorably with those from model compound studies in the literature. Based on these results, it was concluded that the overall rate-limiting step was the oxidation of the sulfonated lignin ring C–C bonds.

## Introduction

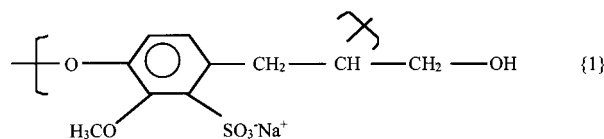
It is clear that supercritical water oxidation (SCWO) can provide a high destruction and removal efficiency for a variety of hazardous aqueous chemical wastes. It has been demonstrated that the process can easily destroy organic wastes at concentrations ranging from 2 to 20 wt %.<sup>1</sup> Treatability studies have also been performed on EPA priority pollutants, industrial wastewaters and sludges (including pulp and paper mill sludges and biological wastes from the pharmaceutical industry), contaminated soils, military wastes, and municipal sludges.<sup>2</sup>

Several literature studies have been performed on the SCWO of model organic compounds using pure oxygen as the oxidant. These studies have focused on the reaction mechanisms involved with the SCWO of these model organic compounds<sup>3–7</sup> and also on developing a global kinetic expression for the SCWO of these model organic compounds.<sup>3–6,8–15</sup> The model compounds employed in these investigations ranged from molecules as simple as CO<sup>11</sup> to phthalic acid.<sup>13</sup> To date, no similar study has been reported in which the SCWO of an industrial wastewater stream that contains a complex mixture of organic compounds had been investigated.

The objective of this study was to investigate the kinetics of the SCWO of a sulfonated lignin waste from an industrial source and to compare the global kinetics expressions obtained from these experiments to those obtained from published model compound studies. An industrial sulfonated lignin wastewater was chosen for this study because polyester fiber represents the largest volume of synthetic fiber used in the textile industry, and the primary aqueous process used to color polyester is disperse dyeing.<sup>16</sup> The primary dispersant used in the disperse dyeing of polyester is sulfonated lignin, which is also a byproduct of chemical pulping processes.<sup>17</sup> After the dyeing process, the dispersing agent remains in the dyebath wastewater and, according to a 1997 report by the U.S. Environmental Protection Agency (EPA), disperse dyeing generates 12–17 gallons of wastewater per

pound of product.<sup>18</sup> Sulfonated lignins also constitute a major component of the Kraft pulping process wastewater, and the EPA estimated in a 1995 report that the production of one ton of pulp requires between 16 000 and 17 000 gallons of water.<sup>19</sup>

Sulfonated lignins are polymers of phenylpropane with methoxyl groups that exhibit polyelectrolyte behavior in an aqueous solution and are very stable chemicals that can be difficult to treat by conventional wastewater treatment methods.<sup>20</sup> The properties of sulfonated lignins can be varied depending on the molecular weight and molecular weight distribution, which is analogous to the distribution of the degree of polymerization or chain length; the degree of sulfonation; and the purity of the product.<sup>20</sup> The typical number-average molecular weight of lignin from the Kraft process is in the range of 3000–5000 with a molecular weight distribution between 3 and 4, and the sulfur content ranges from 2–3 wt %.<sup>21</sup> Although the chemical structure of sulfonated lignins is very complex and only partially understood, a typical sulfonated repeat unit of lignin can be represented by structure {1}.<sup>20,21</sup>



**Kinetic Analysis.** The global kinetics rate equation employed in this work was based on the approach used by Thorton and Savage<sup>3</sup> for the oxidation of model organic compounds and has the form

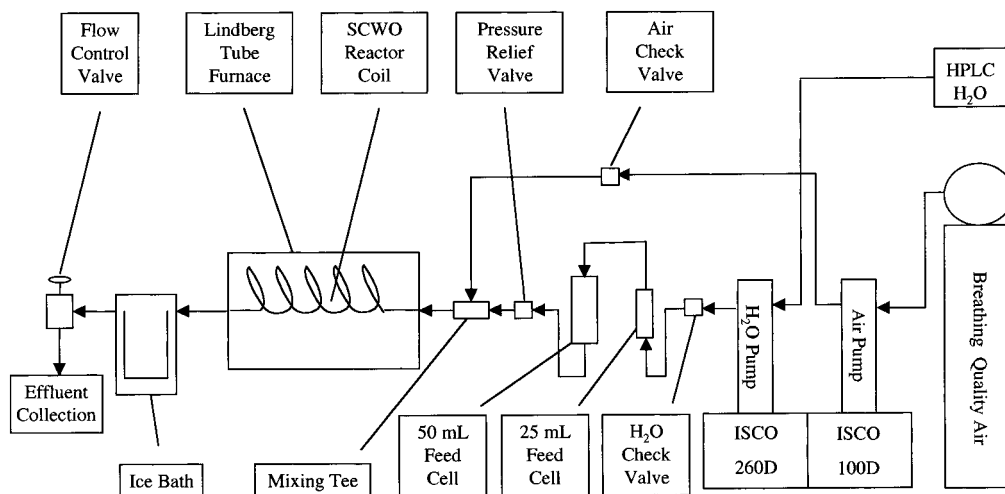
$$r = k[\text{organic}]^a[\text{O}_2]^b[\text{H}_2\text{O}]^c \quad (1)$$

where  $r$  = rate of destruction of organics (M/s);  $k$  = rate constant ( $\text{M}^{1-a-b-c}/\text{s}$ ); and  $a$ ,  $b$ , and  $c$  are the reaction orders.

In eq 1, the organic concentration term can be expressed in terms of initial concentration,  $[\text{organic}]_0$ , and conversion,  $X$ , to give

$$[\text{organic}] = [\text{organic}]_0(1 - X) \quad (2)$$

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**Figure 1.** Schematic diagram of Clemson SCWO system.

Fogler's<sup>22</sup> design equation, which is used to calculate the reactor volume for an isothermal, isobaric plug-flow reactor, relates the rate of destruction,  $r$ , to the conversion,  $X$ , by

$$Q[C]_0 \frac{\partial X}{\partial V} = r \quad (3)$$

where  $Q$  = volumetric flow rate (L/min),  $[C]_0$  = initial concentration (mol/L),  $X$  = conversion, and  $V$  = reactor volume (L).

At a constant and known volumetric flow rate and reactor volume, eq 3 becomes

$$Q[C]_0 \frac{\partial X}{Q \partial \tau} = r \quad (4)$$

where  $\tau$  = residence time (min).

Removing the volumetric flow rate terms from eq 4 results in

$$[C]_0 \frac{\partial X}{\partial \tau} = r \quad (5)$$

Replacing  $[C]_0$  with  $[\text{organics}]_0$  and substituting eqs 1 and 2 into eq 5 gives an expression relating the rate equation for the SCWO of an organic compound to the conversion and reactor residence time for a plug-flow reactor.

$$\frac{\partial X}{\partial \tau} = k[\text{organic}]_0^{a-1}(1-X)^a[\text{O}_2]^b[\text{H}_2\text{O}]^c \quad (6)$$

For experiments in which oxygen and water are present in a large excess, eq 6 can be simplified to<sup>3</sup>

$$\frac{\partial X}{\partial \tau} = k[\text{organic}]_0^{a-1}(1-X)^a[\text{O}_2]_0^b[\text{H}_2\text{O}]_0^c \quad (7)$$

Using the appropriate conversion and residence time data at constant temperature and pressure, the reaction order with respect to the organic compound can be determined using eq 7 by either differential or integral analysis. Similarly, the reaction orders with respect to oxygen and water can be determined. Although the reaction order with respect to oxygen has usually been determined using integral analysis by keeping all variables constant except the initial oxygen concentra-

tion,<sup>23</sup> in this work, differential analysis was used throughout.

### Experimental Section

**Feed Preparation.** An aqueous sulfonated lignin process waste sample was obtained from the Polychemicals Division of Westvaco Corporation, North Charleston, SC. The sample was stored in a sealed 5-gallon bucket, and before samples were taken from the bucket, the solution was mixed via shaking to ensure that any particles that settled out over time were redistributed throughout the solution. The mass fraction of the sulfonated lignin in the waste solution was determined by evaporating the water from five approximately 10-g samples of the waste solution. The waste solutions were added to aluminum pans, and the pans were placed in an oven at 100 °C overnight (Blue M Electric Company, Blue Island, IL, model POM-206 C). The samples were removed from the oven, allowed to cool in a desiccator, and then reweighed. In addition, dried samples of the raw sulfonated lignin waste and a 1000 ppm sulfonated lignin waste solution were sent to Galbraith Laboratories (Knoxville, TN) for elemental analysis to determine the carbon, hydrogen, sulfur, and nitrogen content.

The feed solutions used in the SCWO experiments were prepared by pipetting a calculated volume of the raw sulfonated lignin solution into a volumetric flask and diluting the solution with HPLC-grade water to the total desired volume. The calculated volume of raw sulfonated lignin solution corresponded to the amount of lignin solution needed to produce 2 L of a feed solution that is approximately 1000 ppm in sulfonated lignin. The actual feed concentration for each SCWO experiment was confirmed by measuring the UV spectrum of a 1:10 dilution aliquot.

**SCWO System.** The SCWO system designed for these experiments was a semi-continuous, batch process reactor illustrated schematically in Figure 1. A detailed description of the components and operation of the process is given elsewhere.<sup>24</sup> The water used in the process was Burdick and Jackson (Muskegon, MI) HPLC-grade water. Breathing-quality compressed air (National Welders Supply, Charlotte, NC) was used as the oxygen oxidant source for the SCWO system. This oxygen source was chosen because it alleviated any safety concerns resulting from the use of pure oxygen.

Two feed pumps were used to supply water and air separately to the SCWO process. The pumps were ISCO

Inc. (Lincoln, NE) models 260D and 100DX syringe pumps. The model 260D pump was used control the water flow into the system, and the air was supplied to the system using the model 100DX pump. Both pumps were controlled using an ISCO Series D controller operating in the "modifier" mode. The tubing after each pump was fitted with a flow-check valve from High-Pressure Equipment (Erie, PA) in order to ensure that no air or water could be pulled back into the respective pump, which would have made it impossible to control the oxidant-to-feed ratio.

The water was pumped through two feed cells, 25- and 50-mL cells manufactured by Valco Inc. (Houston, TX), in series. In a previous study by Paradkar et al.,<sup>25</sup> it was found that, by introducing the flow to the top of the feed cells, little dilution occurred during the course of an experiment.

The reaction zone included a coiled tube (reactor) in a Lindberg type 59344 (Watertown, WI) tubular furnace. The furnace had a heater element length of approximately 30 cm and an effectively heated length of approximately 40 cm. The inner diameter of the furnace was approximately 5 cm. K-type thermocouples from Omega Engineering (Stamford, CT), with a temperature range of approximately 0–1250 °C, were used to monitor temperatures in the heated zone. These thermocouples were fixed onto the outer wall of the reactor tubing using Cotronics Corp. type 940 high-temperature adhesive with a maximum temperature of 1093 °C (Brooklyn, NY). The ends of the tube furnace were insulated with glass wool to minimize heat loss. Experimentally, it was determined that the temperature of the reactor could be controlled within  $\pm 5$  °C. The reactors used for the experiments were constructed from 15 000 psi,  $\frac{1}{8}$  in., type 316 stainless steel tubing from High-Pressure Equipment. Four reactors were used in the experiments, specifically, one with no coils, one with 3 coils, one with 6 coils, and one with 9 coils, and the coils had an outer diameter of approximately 5 cm. The reactor lengths were 40, 90, 142.5, and 207 cm for the 0-, 3-, 6-, and 9-coil reactors, respectively.

A micrometering flow control valve from Applied Separations (Allentown, PA) was used to control the flow rate of the system when the pumps were run in the constant-pressure mode. Samples were collected from the flow control valve using prewashed, 24-mL vials supplied by VWR Scientific Products (West Chester, PA).

**SCWO Operation.** To generate the appropriate input data for the kinetics calculations of the SCWO of the sulfonated lignin ring structure, the system temperature, pressure, and residence time were systematically varied. The system pressures used were 195.9, 218, 250.8, 278, and 304.7 atm, which correspond to reduced pressures ( $P_R = P/P_{\text{critical}}$ ) of approximately 0.9, 1.0, 1.15, 1.28, and 1.4, respectively. The temperatures used in the experiments were 310, 407, 455, and 504 °C, which correspond to reduced temperatures ( $T_R = T/T_{\text{critical}}$ ) of 0.9, 1.05, 1.13, and 1.2, respectively. The flow rates used were either 0.25 or 0.5 mL/min, depending on the desired residence time. The combination of the flow rate, the reactor length, and the solution density determined the residence time of the system. The density of water and the compressibility factor of air at the sub- and supercritical conditions used in the experiments was determined using SFSolver<sup>26</sup> and Perry's Chemical Engineering Handbook,<sup>27</sup> respectively. Additionally,

various sulfonated lignin feed concentrations and air concentrations were utilized. Finally, experiments were performed at a  $T_R$  of 1.2 and  $P_R$  of 1.4 with no air feed and a  $T_R$  of 1.2 and  $P_R$  of 1.4 with a 10% nitrogen feed to determine if any significant conversion occurred via either hydrolysis or reaction with the nitrogen present in the air feed.

During an experiment, sample vials were changed every 10 min during the first 40 min of a run. The first 10-min sample was used to ensure that there was good sample flow through the system. After the first 10 min, the oven heaters were turned on. The uncontrolled heating ramp to the desired reaction temperature was usually observed to be approximately 20 min in duration. Samples taken during the first 40 min of the run were visually inspected for a reduction in color to qualitatively determine if the process was working adequately. In addition, the first 40 min of the run were also utilized to allow the pressures and flow rates from the dual pumps to stabilize. While the reactor was at the predetermined final operating conditions, three samples over 20-min intervals were collected. Two additional 10-min samples were collected during the cooling stage after the reactor had been shut down in order to confirm that there was still an adequate flow of the sulfonated lignin feed solution through the system at the end of each kinetics experiment. After each vial change, the elapsed sample collection time, the pump volumes, and the reactor temperature were recorded.

**Sample Analysis.** The UV absorbance maximum at 280 nm of the sulfonated lignin ring structure from the three 20-min reactor effluent samples was used to determine the system outlet ring concentration. The ultraviolet–visible (UV–vis) spectra were collected on a Shimadzu UV-3101 PC UV–vis spectrometer using HPLC-grade water as the reference. Calibration curves of absorbance versus concentration (volume percent) were constructed using 0.25, 0.5, 1.0, 2.0, and 4.0 vol % sulfonated lignin solutions. Volumetric dilution with HPLC-grade water was used to ensure that the absorbance maxima of all of the reactor outlet samples fell within the range of the calibration curves. Because all of the UV measurements on the reactor effluent samples from different experimental trials could not be performed at the same time, the absorbance of a 1% standard solution was used as a control for each data set.

## Results and Discussion

The objective of this research was to study the kinetics of the SCWO of a sulfonated lignin waste and to compare the results of these experiments to those obtained from studies on model organic compounds. Because a sulfonated lignin waste stream represents a complex mixture of compounds, it was necessary to establish a basis on which the kinetic calculations could be performed. Based on the results from preliminary SCWO experiments that demonstrated that the percent conversion was directly related to the loss of color and the decrease in the UV absorbance of the sulfonated lignin, the ring concentration of the reactor effluent samples was chosen as the basis for the kinetic models. To calculate the ring structure concentration, it was assumed that an "average" ring structure structural repeat unit could be used. Therefore, the molecular weight of an average sulfonated lignin repeat structure was calculated from the elemental analysis data and

the average structures for repeat units with structure {1} and without a sulfonate group. For this calculation, the average sulfur content from the elemental analysis of 6.75 wt %, the molecular weight of 259 g/mol for structure {1} (without the Na<sup>+</sup> counterion), and the molecular weight of 180 g/mol for structure {1} without the sulfonate were used. Using these values, the molecular weight of the average structural sulfonated lignin structural repeat unit was calculated to be 216 g/mol or mg/mmol. From the drying experiments, the mass fraction of the sulfonated lignin waste in solution was determined to be  $0.00319 \pm (6.41 \times 10^{-5})$  g/g or  $0.00319 \pm (6.41 \times 10^{-5})$  g/mL, which corresponds to a molar concentration of  $1.48 \pm 10^{-2}$  mol/L (3.19 g/L divided by 216 g/mol). Using this calculated sulfonated lignin solution molar concentration, the UV absorbance could then be expressed in terms of molar concentration of ring structures. Because there is 1 mol of ring structure present per mol of lignin (sulfonated or unsulfonated) repeat unit present, the calculated molar concentration of the sulfonated lignin solution is also equivalent to the molar concentration of ring structures.

**Material Considerations.** To employ an expression such as eq 7 for the kinetic analysis, it was necessary to calculate the actual residence times in the reactor at the specific temperature, pressure, and flow rate conditions employed. In this investigation, the linear velocity of the solution in the reaction zone was used to calculate the residence time. The linear velocity was calculated using the equation

$$v = \frac{Q_{\text{react}}}{A} \quad (8)$$

where  $Q_{\text{react}}$  = the volumetric flow rate of the reaction mixture at the reactor inlet (mL/min),  $v$  = linear velocity of the fluid (cm/min), and  $A$  = internal cross-sectional area of the tubing (cm<sup>2</sup>).

The residence time was then calculated using the equation

$$\tau = \frac{L}{v} 60 \quad (9)$$

where  $\tau$  = residence time (s) and  $L$  = reactor tube length (cm).

The molar densities of water, calculated using the SFSolver<sup>26</sup> software, and air, calculated using the appropriate compressibility factors,<sup>27</sup> were used to compute the volumetric flow rate of the reaction mixture solution for a specific experiment. Because the inlet stream to the reactor outlet section and the outlet stream of the reactor inlet section are at the same process conditions and molar flow rates, the volumetric flow rates at the reactor inlet and the reactor outlet will be the same. Consequently, the molar flow of the ring structure at the system outlet ( $M_{\text{Rout}}$ ) and the solution volumetric flow rate at the reaction conditions can be used to calculate the molar concentration of ring structure leaving the reactor using eq 10.

$$[R] = \frac{M_{\text{Rout}}}{Q_{\text{React}}} \quad (10)$$

Finally, the conversion,  $X$ , of ring structure data was calculated using the following relation:

$$X = \frac{[R]_0 - [R]}{[R]_0} \quad (11)$$

where  $[R]_0$  = the inlet concentration of ring structure (mmol/mL) and  $[R]$  = the outlet concentration of ring structure, (mmol/mL).

Expressed in terms of the inlet concentration of ring structure  $[R_0]$  and the conversion,  $X$ , the kinetic expression in eq 7 thus becomes

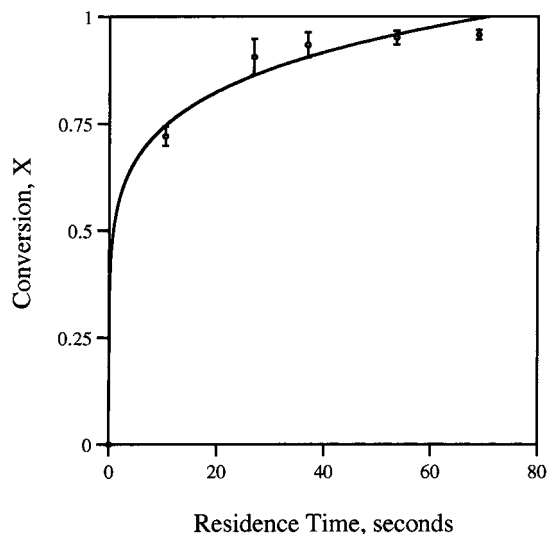
$$\frac{\partial X}{\partial \tau} = k[R]_0^{a-1} (1 - X)^a [O_2]_0^b [H_2O]_0^c \quad (12)$$

**Ring Structure Reaction Order.** The conditions selected for the experiments conducted to determine the reaction order,  $a$ , with respect to the ring structure, a reduced temperature of 1.2 (504 °C) and a reduced pressure of 1.4 (304.7 atm), were chosen because any instantaneous variations in the temperature and pressure of the system would have only a small effect on the reduced density of water. The feed solution concentrations employed were 460, 940, and 1380 ppm. At the 10 vol % of air used, the molar excess oxygen concentrations were 885, 381, and 227%, respectively. The water flow rates used were ~0.25 and 0.5 mL/min, and the 0-, 3-, 6-, and 9-coil reactor tubes were used. The residence time and percent conversion data used to calculate the reaction order with respect to the ring structure,  $a$ , are summarized in Table 1. All of the values reported in Table 1 reflect the average of the three samples collected over 20-min intervals during one experimental trial. In these experiments, the calculated reactor residence times ranged from 9.8 ( $\pm 1.6$ ) s to 107.0 ( $\pm 14.0$ ) s, and the measured conversions ranged from 0.511 ( $\pm 0.026$ ) to 0.958 ( $\pm 0.011$ ). An examination of all of the standard deviation data summarized in Table 1 would suggest that, under these experimental conditions, the reactor residence times were generally reproducible to less than  $\pm 2.5$  s. Probably the most significant factor affecting the residence time reproducibility was the difficulties experienced with the manual system flow control valve at the exit end of the system. This valve had to be constantly adjusted during a run in order to maintain the targeted flow rate for the experiment. Perhaps, more importantly, the standard deviation data for both the residence times and conversions reveal no relationship between variability and either the number of coils in the reactor or the average flow rates.

Prior to the actual kinetic analysis of the conversion versus residence time data, control experiments were conducted to determine if a hydrolysis reaction between the water and the sulfonated lignin waste or the presence of N<sub>2</sub> significantly affected the conversion of the ring structure. These experiments were conducted using the 460 ppm sulfonated lignin solution at a temperature of 504 °C and a pressure of 304.7 atm using the 9-coil reactor. These conditions were chosen because the conversion of the ring structure observed for the 460 ppm sulfonated lignin solution in the 10 vol % flow of air experiments was >0.95. At a calculated residence time of 54.0 ( $\pm 3.1$ ) s, the conversion from the hydrolysis reaction alone was calculated to be 0.046 ( $\pm 0.015$ ). Under the same conditions but with a vol % flow of nitrogen at a calculated residence time of 51.9 ( $\pm 2.6$ ) s, the conversion from this hydrolysis reaction was calculated to be 0.039 ( $\pm 0.028$ ). Both of these values were less than 5% of the conversion that occurred in the

**Table 1. Summary of the Average Residence Time and Conversion Data for the SCWO of 460, 940 and 1380 ppm Sulfonated Lignin Solutions at 304.7 atm and 504 °C**

460 ppm		940 ppm		1380 ppm	
residence time (s)	conversion	residence time (s)	conversion	residence time (s)	conversion
10.4 (±2.0)	0.721 (±0.023)	9.9 (±0.8)	0.500 (±0.019)	9.8 (±1.6)	0.511 (±0.026)
26.9 (±5.7)	0.906 (±0.042)	24.2 (±2.5)	0.793 (±0.011)	23.3 (±0.7)	0.746 (±0.009)
36.9 (±1.8)	0.934 (±0.029)	43.7 (±0.8)	0.851 (±0.039)	35.4 (±0.3)	0.801 (±0.028)
53.5 (±1.5)	0.951 (±0.016)	52.7 (±1.3)	0.896 (±0.010)	51.7 (±0.2)	0.856 (±0.017)
68.9 (±1.9)	0.958 (±0.011)	68.9 (±13.6)	0.911 (±0.036)	67.1 (±10.2)	0.882 (±0.026)
		107.0 (±14.0)	0.941 (±0.011)	101.3 (±3.1)	0.930 (±0.019)

**Figure 2.** Comparison of experimental and power law curve fit conversion vs residence time data for SCWO of 460 ppm sulfonated lignin solution.

presence of an oxidant. These data clearly demonstrate that the conversion observed in these experiments results predominantly from the SCWO of the ring structures.

For each set of data in Table 1, a differential analysis of the data was used to determine the reaction order with respect to the ring structure concentration,  $a$ . The data for the 460 ppm experiments will be used to illustrate the analysis. The first step involved curve fitting the residence time versus conversion data in Table 1. The best fit for the 460 ppm data set was found to be a three-parameter power law curve with

$$X = 0.5401\tau^{0.1434} - 0.0006 \quad (13)$$

and an  $r^2$  value of 0.99. The residence time versus conversion data and power law curve fit for the 460 ppm data are shown in Figure 2.

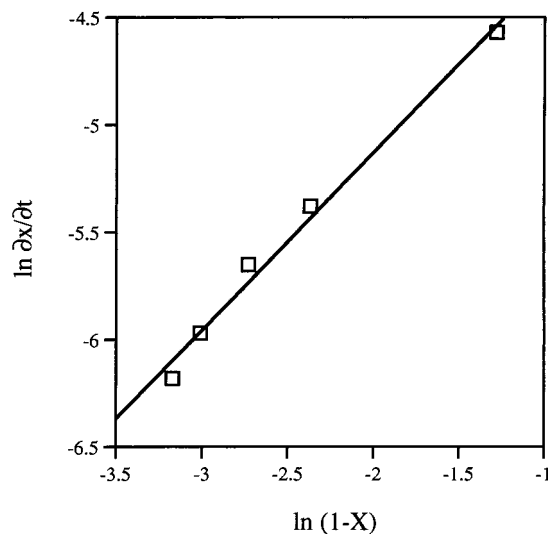
Taking the natural logarithm of eq 12 and rearranging results in the expression

$$\ln\left(\frac{\partial X}{\partial \tau}\right) = a \ln(1 - X) + \ln(k[R]_0^{a-1}[O_2]_0^b[H_2O]_0^c) \quad (14)$$

which can be used to determine the value of the reaction order with respect to the ring structure concentration by plotting  $\ln(\partial X/\partial \tau)$  versus  $\ln(1 - X)$ , with the slope of the resulting line being equal to  $a$ . Differentiating eq 13 with respect to time yields

$$\frac{\partial X}{\partial \tau} = 0.5401 \times 0.1434 \times \tau^{(0.1434-1)} \quad (15)$$

The value of  $\partial X/\partial \tau$  was calculated for each residence time

**Figure 3.** Plot and linear regression of 460 ppm  $\ln(\partial X/\partial \tau)$  versus  $\ln(1 - X)$  data.

using eq 15, and then the  $\ln(\partial X/\partial \tau)$  versus  $\ln(1 - X)$  data were plotted and fitted with a linear regression to determine the value of  $a$ , as shown in Figure 3. The  $r^2$  value for the regressed line was 0.99, and the resulting value for the reaction order with respect to the ring structure,  $a$ , was 0.829.

A similar data analysis was carried out for the 940 and 1380 ppm data. The  $r^2$  for the best-fit three-parameter power law equation for the 940 ppm data was 0.97 and that for the 1380 ppm data was 0.96. The corresponding reactions orders with respect to the ring structure,  $a$ , were 0.868 and 0.986, respectively.

In the literature, the reported values for the reaction order with respect to the organic compound for the SCWO of various simple, low-molecular-weight compounds range from 0.47 to 1.23. However, investigations involving a data analysis technique similar to the one used in this study have reported values of the reaction order with respect to the organic compound ranging from 0.88 to 1. Specifically, the SCWO studies conducted by Thornton and Savage<sup>3</sup> using phenol resulted in a reported value of 1 for the reaction order of phenol. Crain et al.<sup>7</sup> and Li et al.<sup>4</sup> reported values of 1 and 0.88 for the SCWO of pyridine and 2-chlorophenol, respectively. Other values reported for aromatic ring systems include 0.53 for phthalic acid<sup>13</sup> and 0.97 for 2,4-dichlorophenol.<sup>14</sup> In this investigation of the SCWO of sulfonated lignin waste, the average reaction order with respect to the ring structure,  $a$ , was determined to be  $0.886 \pm 0.066$ , which is consistent with these literature values. Based on the small deviation of the reaction orders reported by Thornton and Savage,<sup>3</sup> Crain et al.,<sup>7</sup> and Li et al.<sup>4</sup> and also found in this study, these data suggest that the global kinetics SCWO reaction order

**Table 2. Summary of the Average Residence Time and Conversion Data for the SCWO of 460 ppm Sulfonated Lignin Solutions at 7.5, 5.0, and 2.5 vol % Air**

7.5 vol % air		5.0 vol % air		2.5 vol % air	
residence time (s)	conversion	residence time (s)	conversion	residence time (s)	conversion
23.1 (±3.1)	0.793 (±0.041)	22.7 (±1.1)	0.745 (±0.042)	23.7 (±2.4)	0.608 (±0.044)
32.9 (±3.1)	0.830 (±0.040)	37.1 (±1.0)	0.808 (±0.056)	35.5 (±4.4)	0.662 (±0.049)
53.0 (±2.3)	0.894 (±0.017)	45.4 (±1.1)	0.873 (±0.041)	50.9 (±4.3)	0.782 (±0.010)

with respect to the organic compound could be independent of the specific organic compound. Although no mechanism or effluent characterization experiments were conducted in this investigation, the similarities between reaction orders suggests that the rate-limiting step in the SCWO of sulfonated lignin is similar to the rate-limiting step in the SCWO phenol and 2-chlorophenol, which is the cleavage of the carbon-carbon bonds in the phenolic ring structure.

**Oxygen Reaction Order.** The conditions chosen to determine the reaction order with respect to oxygen,  $b$ , were also a reduced temperature of 1.2 (504 °C) and reduced pressure of 1.4 (304.7 atm). The nominal fluid flow rate employed was 0.5 mL/min. The flow out of the SCWO system proved to be very difficult to control when the air fed to the system was greater than 10 vol %. Therefore, a feed cell concentration of sulfonated lignin waste was chosen that would allow for significant excess oxygen to be present over as wide a range of experimental conditions as possible. Based on the previous results, it was believed that any concentration below 460 ppm would result in complete conversion and, if complete conversion occurred, the actual reactor residence time at which complete ring structure destruction was achieved would not be known. Consequently, a feed cell concentration of 460 ppm of the sulfonated lignin waste was selected for the experiments used to determine the reaction order with respect to oxygen,  $b$ . In addition to using the data from the 10r vol % air flow samples previously discussed, experiments were performed at 7.5, 5.0, and 2.5 vol % flow rates. These values correspond to  $[O_2]_0$  molar concentrations of  $0.030 \times 10^{-4}$ ,  $0.022 \times 10^{-4}$ ,  $0.015 \times 10^{-4}$  and  $0.0073 \times 10^{-5}$  and excess molar oxygen concentrations of 872, 607, 360 and 126%, respectively. The residence time and percent conversion data used to calculate the reaction order with respect to oxygen,  $b$ , for the additional experiments carried out at 7.5, 5.0, and 2.5 vol % air experiments are summarized in Table 2. All of the values reported in Table 2 are the average of the three samples collected over 20-min intervals during one experimental trial. Simple inspection of the data summarized in Table 2 clearly shows, that at each residence time, as the volume percent of air was increased, the conversion increased, which strongly suggests that oxygen has a reaction order greater than zero. To calculate the reaction order with respect to oxygen,  $b$ , eq 14 was first rearranged to give

$$\ln\left(\frac{\partial X}{\partial \tau}\right) - (a - 1) \ln([R]_0) - a \ln(1 - X) = b \ln([O_2]_0) + \ln(k[H_2O]_0^c) \quad (16)$$

Then, the left-hand side of eq 16 was set equal to  $y$ , yielding

$$y = b \ln([O_2]_0) + \ln(k[H_2O]_0^c) \quad (17)$$

Using eq 17, a plot of  $y$  versus the  $\ln([O_2]_0)$  should yield a straight line with a slope of  $b$ , the reaction order with respect to oxygen. The average value of the ring structure reaction order,  $a$ , of  $0.886 \pm 0.066$  from the previous section was used in all of the calculations of the oxygen reaction order. In addition, each of the three different residence times ( $\sim 25$ ,  $\sim 35$ , and  $\sim 50$  s), which correspond to the use of the 3-, 6-, and 9-coil reactor tubes, respectively, at each oxygen concentration was considered as constituting a separate data set for the determination of the oxygen reaction order,  $b$ .

The linear fit of the  $y$  versus  $\ln([O_2]_0)$  data for the 3-coil reactor (25 s) resulted in a value of 0.752 for  $b$  with an  $r^2$  value of 0.907, that for the 6-coil reactor (35 s) resulted in a value of 0.875 for  $b$  with an  $r^2$  value of 0.872, and that for the 9-coil reactor (25 s) resulted in a value of 0.802 for  $b$  with an  $r^2$  value of 0.880. The average value of  $b$  calculated from the three data sets was 0.810 with a standard deviation of 0.062.

In one of the kinetic studies conducted on the SCWO of small, low-molecular-weight organic compounds, the reaction order with respect to oxygen was assumed to be 0.<sup>11</sup> In other investigations, the reported values for the reaction order with respect to oxygen have ranged from -0.33 to 1.16, with the majority of these values near 0.5 for the various data analysis methods employed.<sup>4-7,10,12,14,15,23</sup> Except for the value of 1.16 from the 2,4-dichlorophenol study by Lin et al.,<sup>14</sup> these values of the reaction order with respect to oxygen are significantly lower than the 0.81 value for the oxygen reaction order found in this study. Whether these results suggest that the SCWO of a more complex, high-molecular-weight compound is more dependent on the oxygen concentration of the system than the model compounds or whether it simply reflects differences in the experimental approaches is not known at this time.

**Water Reaction Order.** To change the water concentration in the system for the determination of the water reaction order,  $c$ , the pressure was varied. As the pressure under supercritical conditions is varied at constant temperature, the density of the water changes, which in turn significantly changes the volumetric flow rate as well as the residence time in the reactor tube. To compensate for the change in the volumetric flow rate with pressure, different reactors were used to offset the changes in the volumetric flow rate dependent upon the target residence time. The data used to calculate the reaction order with respect to water,  $c$ , included the results of the 460 and 940 ppm, 304.7 atm, 504 °C with a 10 vol % air flow experiments, as well experiments in which the pressure was varied down to a slightly subcritical level at 195.9 atm. The experiments and relevant experimental data used to determine the reaction order with respect to water,  $c$ , are summarized in Table 3. That the pressure, and consequently the  $[H_2O]_0$ , has an effect on the conversion can be illustrated by comparing some selected data from Table 3. Comparing the conversion for the 460 ppm data at residence

**Table 3. Summary of the Data Used to Determine the Reaction Order with Respect to Water, *c*, for the SCWO of 460 and 940 ppm Sulfonated Lignin Solutions**

feed cell concentration (ppm)	pressure (atm)	reactor coils	[H <sub>2</sub> O] <sub>0</sub> (M)	residence time (s)	conversion ( <i>X</i> )
460	304.7	3	6.302 (±0.002)	26.9 (±5.7)	0.906 (±0.042)
460	304.7	6	6.304 (±0.001)	36.9 (±1.8)	0.935 (±0.029)
940	304.7	3	6.305 (±0.000)	24.2 (±2.5)	0.793 (±0.011)
460	278.0	3	5.618 (±0.005)	20.9 (±0.7)	0.864 (±0.025)
460	278.0	6	5.615 (±0.001)	35.4 (±3.9)	0.905 (±0.025)
940	278.0	3	5.615 (±0.005)	20.1 (±0.8)	0.722 (±0.011)
460	250.8	6	4.926 (±0.001)	28.3 (±1.1)	0.874 (±0.063)
460	250.8	9	4.926 (±0.001)	40.5 (±2.4)	0.898 (±0.028)
940	250.8	6	4.925 (±0.001)	28.5 (±1.4)	0.719 (±0.024)
460	219.0	6	4.715 (±0.001)	26.8 (±0.4)	0.843 (±0.015)
460	219.0	9	4.715 (±0.001)	38.0 (±3.5)	0.885 (±0.032)
940	219.0	6	4.715 (±0.002)	27.8 (±2.9)	0.700 (±0.021)
460	195.9	6	3.653 (±0.001)	21.7 (±1.3)	0.744 (±0.031)
460	195.9	9	3.654 (±0.000)	31.1 (±1.9)	0.820 (±0.044)
940	195.9	6	3.653 (±0.001)	21.9 (±2.0)	0.501 (±0.025)

times of 36.9, 35.4, 40.0 and 38.0 s, *X* decreases from 0.935 to 0.885 as the pressure decreases from 304.7 to 219.0 atm. Similarly, comparing the conversion for the 940 ppm data at residence times of 24.2, 20.1, 28.5, 27.8, and 21.9 s, *X* decreases even more significantly from 0.793 to 0.501 as the pressure decreases from 304.7 to 195.9.

The procedure used to calculate the reaction order with respect to water, *c*, was similar to that employed to determine *b*. Equation 14 was first rearranged once again, and then the left-hand side of the equation was set equal to *z*, which yields eq 18.

$$z = c \ln([\text{H}_2\text{O}]_0) + \ln(k) \quad (18)$$

To calculate the values for *z*, the average values for *a* (0.866) and *b* (0.810) as well as the experimental data from Table 3 were used. The linear fit from the plot of *z* versus the  $\ln([\text{H}_2\text{O}]_0)$  was then used to determine the reaction order with respect to water, *c*. In addition, the results for the two different residence times for the 460 ppm sulfonated lignin solution experiments at each pressure and the 940 ppm sulfonated lignin solution experiments at each pressure were treated as separate data sets for the determination of the water reaction order.

The linear regression of *z* vs  $\ln([\text{H}_2\text{O}]_0)$  for the 460 ppm sulfonated lignin solution experiments at the residence times of ~25 s resulted in a value of 0.662 for *c* with an *r*<sup>2</sup> of 0.915. The 460 ppm sulfonated lignin solution experiments at the residence times of ~35 s gave a value of 0.606 for *c* with an *r*<sup>2</sup> of 0.955, and for the 940 ppm solution experiments, the corresponding value of *c* was found to be 0.644 with an *r*<sup>2</sup> of 0.883. The average value of *c* obtained using the three data sets was  $0.637 \pm 0.029$ .

In most of the previous kinetic studies, the reaction order with respect to water either was not calculated or it was assumed to be zero. Only in three of the previous studies did the authors attempt to experimentally determine the reaction order with respect to water. Thorton and Savage<sup>3</sup> reported a reaction order of 0.7 for water for the SCWO of phenol, Li et al.<sup>4</sup> reported a value for the reaction order with respect to water of 0.34 for the SCWO of 2-chlorophenol, and Ahn et al.<sup>13</sup> reported a water reaction order of 0.53 for the SCWO of phthalic acid. Clearly, the value for the reaction order with respect to water, *c*, reported in this investigation,

0.637, is well within the range of the values reported by Thorton and Savage<sup>3</sup> and Li et al.<sup>4</sup> using similar data analysis techniques, as well as being within the range of that reported by Ahn et al.<sup>13</sup>

**Arrhenius Parameters.** It is difficult to assign any true physical significance to the Arrhenius parameters determined in a study such as the one reported here where a global kinetics expression has been derived for the SCWO of a complex mixture. It has been suggested that the preexponential factor and activation energy could merely be empirical figures to account for changes in temperature.<sup>22</sup> This would suggest that the Arrhenius parameters determined from a specific study might only be valid for that particular investigation. Otherwise, it is possible that the global activation energy is the total of the activation energies from each reaction step involved in the global reaction and, therefore, is dependent on the reaction mechanism. This interpretation would imply that, if the global activation energies are to be compared, then the reaction mechanisms of different compounds must be identical. In this study, the Arrhenius parameters were determined simply to characterize the effect of temperature on the overall kinetics of the reactions.

Because the rate constant of a reaction is constant for all residence times and conversions, only conversion data at a specific residence times and temperatures were needed to calculate the Arrhenius parameters. In addition to the 304.7 atm, 504 °C, 10 vol % air experiments that have previously been discussed, new experiments were performed at temperatures of 504, 455, 407, and 310 °C, which correspond to reduced temperatures of approximately 1.2, 1.13, 1.05, and 0.9, with the water density at the reaction conditions ranging from 117 to 602 mg/mL, respectively. The calculated residence times, measured conversions, and average reaction temperatures used to determine the Arrhenius parameters are summarized in Table 4.

The Arrhenius parameters, *A* and *E<sub>a</sub>*, are related to the temperature of a reaction and the rate constant, *k*, by

$$k = A e^{-(E_a/RT)} \quad (19)$$

where *k* = rate constant (M<sup>1-*a*-*b*-*c*</sup>/s), *A* = preexponential constant (M<sup>1-*a*-*b*-*c*</sup>/s), *E<sub>a</sub>* = activation energy (kJ/mol), *R* = gas constant [kJ/(mol K)], and *T* = temperature (K).

**Table 4. Summary of the Data Used to Determine the Arrhenius Parameters for the SCWO of 460 and 940 ppm Sulfonated Lignin Solutions**

feed cell concentration (ppm)	$T$ (°C)	reactor coils	residence time (s)	conversion ( $X$ )
460	504 (±2.5)	3	26.9 (±5.7)	0.906 (±0.042)
460	504 (±2.0)	6	36.9 (±1.8)	0.935 (±0.029)
940	504 (±2.0)	6	43.7 (±0.8)	0.851 (±0.039)
460	452 (±2.5)	3	30.1 (±2.1)	0.893 (±0.016)
460	454 (±1.5)	6	43.2 (±1.0)	0.923 (±0.035)
940	458 (±0.6)	6	44.9 (±2.9)	0.814 (±0.023)
460	405 (±1.0)	3	58.8 (±1.5)	0.614 (±0.052)
460	407 (±2.1)	6	99.0 (±4.4)	0.743 (±0.025)
940	405 (±2.3)	6	91.5 (±4.4)	0.580 (±0.028)
460	306 (±6.1)	3	111.3 (±17.4)	0.297 (±0.045)
460	310 (±3.5)	6	183.6 (±3.3)	0.417 (±0.064)
940	308 (±1.5)	6	171.0 (±11.8)	0.250 (±0.052)

Taking the natural logarithm of eq 19 and rearranging yields

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad (20)$$

To calculate the natural logarithm of the rate constant, eq 14 was rearranged to give

$$\ln\left(\frac{\partial X}{\partial \tau}\right) - (a-1) \ln([R]_0) - a \ln(1-X) - b \ln([O_2]_0) - c \ln([H_2O]_0) = \ln(k) \quad (21)$$

Using eq 21, a plot of the natural log of the rate constant,  $k$ , versus the reciprocal temperature has a slope equal to the negative of the activation energy divided by the gas constant,  $-E_a/R$ , and an intercept equal to the preexponential factor,  $A$ . The average values of  $a$  (0.866),  $b$  (0.810), and  $c$  (0.637) and the experimental conversion data were used to determine the value of  $\ln(k)$ . In addition, the two different reactor coil experiments for the 460 ppm and the 940 ppm sulfonated lignin solution experiments at each temperature were considered as constituting separate data sets for the determination of the Arrhenius parameters,  $E_a$  and  $A$ .

The plot of the  $\ln(k)$  versus  $T^{-1}$  data from the data for the 460 ppm solution in the 3-coil reactor yielded a linear regression line with a slope of 100.7 kJ/mol ( $E_a$ ) and intercept of  $10^{5.74} M^{1-a-b-c}/s$  ( $A$ ) with an  $r^2$  of 0.93. The slope of the linear regression line from the 6-coil reactor data was 109.5 kJ/mol and the intercept was  $10^{6.36} M^{1-a-b-c}/s$  with an  $r^2$  of 0.93, while the 6-coil, 940 ppm sulfonated lignin solution regression line had a slope of 92.7 kJ/mol, an intercept of  $10^{4.87} M^{1-a-b-c}/s$ , and an  $r^2$  of 0.93. The average activation energy,  $E_a$ , for the SCWO of the sulfonated lignin solutions obtained from these experiments was  $100.9 \pm 8.4$  kJ/mol and the average preexponential factor,  $A$ , for the SCWO of sulfonated lignin waste was  $10^{5.66(\pm 0.75)} M^{1-a-b-c}/s$ . These results clearly suggest that the global kinetics of the SCWO of these sulfonated lignin solutions exhibit the expected temperature dependence and, consequently, are similar to those of the model compounds that have been studied previously. The values reported here are also consistent with those from the literature.<sup>3-5, 13,14</sup>

**Evaluation of the Overall Rate Expression.** After each of the individual kinetic parameters that affect the rate of conversion of the sulfonated lignin solution was calculated, the overall global kinetics expression was

evaluated. Because each of the reactions orders,  $a$ ,  $b$ , and  $c$ , was determined using a different data set, the criterion used for this evaluation was how well the predicted conversions calculated using the rate equation compared to the actual experimental reaction. Substituting the calculated values for the reaction order with respect to the ring structure,  $a$ , the reaction order with respect to oxygen,  $b$ , the reaction order with respect to water,  $c$ , and the Arrhenius parameters,  $A$  and  $E_a$ , into eq 1 resulted in the rate eq 22

$$\frac{\partial [R]}{\partial \tau} = 10^{5.66 \pm 0.75} e^{-12140 \pm 1000/T} [R]^{0.886 \pm 0.066} [O_2]^{0.810 \pm 0.062} [H_2O]^{0.637 \pm 0.029} \quad (22)$$

which, in terms of conversion, yielded the expression in eq 23.

$$\frac{\partial X}{\partial \tau} = 10^{5.66 \pm 0.75} e^{-12140 \pm 1000/T} [R]_0^{(0.886 \pm 0.066)} (1-X)^{0.886 \pm 0.066} [O_2]_0^{0.810 \pm 0.062} [H_2O]_0^{0.637 \pm 0.029} \quad (23)$$

Rearranging eq 23, integrating using the limit of  $X=0$  at  $\tau=0$ , and solving for  $X$  resulted in

$$X = 1 - (1 - 0.114 \times 10^{5.66} e^{-12140/T} [R]^{-0.114} [O_2]^{0.810} [H_2O]^{0.637} \tau)^{8.77} \quad (24)$$

Equation 24 was then used to calculate the predicted conversion based on the calculated molar concentrations, temperatures, and residence times for each data set.

The residence times, experimental conversions, and the calculated conversions for the 460 and 1380 ppm sulfonated lignin solution experiments conducted at 304.7 atm and 504 °C with a 10 vol % flow of air are summarized in Table 5.

As illustrated by the results summarized in Table 5, the rate equation does not predict the conversion of the 460 ppm sulfonated lignin solution very well until higher residence times are achieved. This would suggest that the power law curve fitted to the experimental data in the determination of the reaction order with respect to the ring structure does not model conversion well at lower residence times. One reason for this may be the lack of low-residence-time and low-conversion data in the determination of  $a$  where the rate of change of conversion with residence times below 20 s is greatest. This conclusion is further supported by the 1380 ppm results for which only the predicted conversions at residence times shorter than 30 s are not within  $\pm 5\%$  or very close to the predicted conversions. Again, as for the cases of the 460 ppm solution data, the lack of low-conversion and low-residence-time data could have resulted in a curve fit that does not accurately reflect the experimental conversion at short residence times. On the other hand, the shapes of the curves in Figure 6 suggest that the overall kinetic model does do a reasonable job of reflecting the actual experimental relationship between residence time and conversion. Finally, because all of the other kinetic parameters were based on the determination of  $a$ , some of the offset observed in the data in Table 5 could probably be attributed to the effects of the other reaction orders and the Arrhenius parameters on the calculated conversions. This effect may also have contributed to the generally

**Table 5. Summary of the Experimental and Calculated Conversions for the SCWO of the 460 and 1380 ppm Sulfonated Lignin Solutions at 304.7 atm and 504 °C**

460 ppm			1380 ppm		
residence time (s)	experimental conversion	calculated conversion	residence time (s)	experimental conversion	calculated conversion
10.4	0.721	0.326	9.8	0.511	0.275
26.9	0.906	0.653	23.3	0.746	0.546
36.9	0.935	0.770	35.4	0.801	0.731
53.5	0.951	0.889	51.7	0.856	0.844
68.9	0.958	0.951	67.1	0.882	0.919
—	—	—	101.3	0.930	0.983

lower  $r^2$  (~0.9) values observed in the curve fits for the  $b$  and  $c$  reaction order determinations.

## Conclusions

The average value determined for the ring structure reaction order,  $a$ , was  $0.886 \pm 0.066$ , which is consistent with literature values reported for the SCWO of model compounds that contain a phenolic ring structure. Comparing the results of this investigation to other reports in the literature suggests that the rate-limiting step in the SCWO of sulfonated lignin waste is similar to the rate-limiting step reported for the SCWO of model phenolic compounds and is probably related to the cleavage of the carbon-carbon bonds in the ring structure. The average value obtained for the oxygen reaction order,  $b$ , was  $0.810 \pm 0.062$ , which is higher than values for  $b$  reported in the literature, which could indicate that the rate of the SCWO of a complex, high-molecular-weight compound might be more oxygen-dependent. The average value obtained for the reaction order with respect to water,  $c$ , was  $0.637 \pm 0.026$ , which is well within the range of the previously reported literature values. The average values obtained for the Arrhenius parameters,  $E_a$  and  $A$ , were  $100.9 \pm 8.4$  kJ/mol. and  $10^{5.66(\pm 0.75)} \text{ M}^{1-a-b-c}/\text{s}$ , respectively. These values are also consistent with those reported in the literature for model compounds studies.

Good agreement was observed between the predicted global kinetics model and the actual experimental conversion as a function of reactor residence time, except at the shorter residence times. As a result of these comparisons, it was concluded that the derived global kinetic model could predict all of the experimentally observed effects of temperature, pressure, feed concentration, and residence time on the overall conversion for the SCWO of the sulfonated lignin solutions. It was also concluded that the assumptions made in the development of the model were valid and suggests that similar approaches could be taken in order to study the SCWO of other complex waste streams. In addition, the results of this investigation demonstrate that air can be successfully utilized as the oxidant source in SCWO kinetic studies. It was also concluded that, in order to improve the overall global kinetic expression, more data at low conversions and short residence times would be needed because of the effect that the ring structure reaction order,  $a$ , has on the other derived kinetic parameters.

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