

# Analysis of High-Pressure, Multiphase, Batch Reactor Data

A new model for prediction of the liquid-phase concentration of a sparingly soluble, volatile hydrocarbon under wet-air oxidation conditions.

R. S. Willms, A. M. Balinsky, D. D. Reible, D. M. Wetzel, and D. P. Harrison, Louisiana State University, Baton Rouge, La. 70803-7303

Disposal of hazardous and toxic wastes has historically meant storage in landfills or similar facilities. Due to the widely publicized contamination problems associated with some storage facilities and to the Resource Conservation and Recovery Act, increasing emphasis has been placed in recent years on the ultimate destruction of hazardous wastes. At the current time, the most commonly used ultimate disposal method is incineration. For wastes containing in excess of 30% combustible organic matter, incineration is both effective and relatively inexpensive. More dilute wastes, however, typically require heating and vaporization of large quantities of water. The expense of providing the additional energy requirements for dilute wastes has provided the impetus to identify alternative destruction methods.

Among the host of alternative destruction methods that have been proposed is wet-air oxidation. Wet-air oxidation is a semi-commercial process that has been used to treat a variety of weakly toxic chemical wastes and for the regeneration of activated carbon. As the name implies, wet-air oxidation is the destructive oxidation of waste compounds by dissolved oxygen in a moderate temperature (130-400°C) aqueous phase. The source of the dissolved oxygen is compressed air. The process operates at pressures of 1000-3000 psi (6.89-20.9 MPa) to reduce vaporization of the aqueous phase, and raise the equilibrium dissolved-oxygen content of the reaction medium. Thus, wastes that are dilute, e.g. 1-30% oxidizable waste, can be economically destroyed without a prior dewatering step. The moderate temperatures of wet-air oxidation, however, result in long reaction times. Minutes or hours are required for the reaction as opposed to seconds required for incineration.

Any attempt to balance the costs of residence time and energy requires an accurate description of the oxidation kinetics for the compound or waste stream in question. Many previous kinetics studies can be faulted in that non-specific measures of the reaction efficiency have been employed, such as oxygen demand reduction and percent destruction of the test compound after a given time period. Transient kinetic measurements are required to describe the reaction rate and reaction mechanism, both requirements for development of an optimal process design.

Due to the sampling technique and the inherent nature of the wet-air oxidation process, a variety of potential problems with the interpretation and analysis of the raw concentration-time data become apparent. These include vapor-liquid equilibrium effects, the effects of sample withdrawal from the batch reactor, and density variations between reactor and sample injector. Corrections for each of these effects must be incorporated into the analysis in order to extract the inherent kinetic information. The ob-

jectives of this paper are to identify these complicating factors, indicate their effects, and develop a methodology for the determination of true kinetic parameters from raw data. To illustrate the effectiveness of the resulting model, first order reaction rate constants are determined from *m*-xylene data. These constants are compared to ones computed using traditional analysis techniques.

## EXPERIMENTAL

### Equipment

Figure 1 shows the experimental apparatus. All materials touching reaction fluids were 316 stainless steel. The 1 liter Autoclave Engineers reactor, fitted with a variable speed "MagneDrive" stirrer and an electric furnace, served as the reaction vessel. It is rated to 343°C and 5000 psi (34.5 MPa). An Autoclave Engineers temperature controller generally held the temperature to within  $\pm 2^\circ\text{C}$  of setpoint.

The Valco, Inc. sampling valve allowed the injection of  $1\mu\text{l}$  samples into the GC. Its key component is a polymer seal with  $1\mu\text{l}$  grooves which, when rotated, vaporized the high pressure liquid reactor sample into the low pressure GC carrier gas stream. The severe duty of high temperature and pressure resulted in rapid erosion of both the high and low temperature polymer materials usually supplied by Valco. The most satisfactory results were realized by using what Valco calls "injection molded Valcon-H" polymer, only obtained on special request. The valve was equipped with a heater and controller to maintain the desired temperature. The tubing leading from reactor to valve and from valve to GC were maintained at the valve

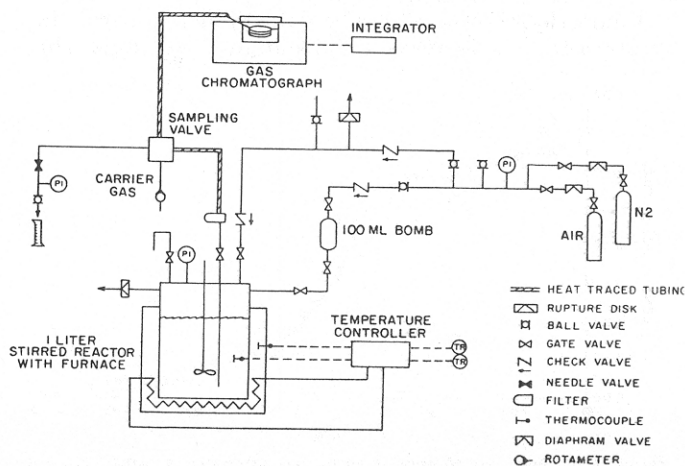


Figure 1. Experimental apparatus.

temperature with heating tape. A 2 $\mu$  Nupro in-line filter kept solids from reaching the valve.

A Perkin-Elmer model 990 gas chromatograph equipped with dual flame ionization detectors analyzed the reactor samples, with results recorded and processed on a Hewlett Packard Model 3390A integrator. For all the GC work the following parameters applied: carrier gas—helium; carrier gas flowrate — 30 ml/min; valve temperature — 150°C; column temperature — 90°C isothermal; manifold temperature — 250°C. The GC column was 6 ft  $\times$  1/4 in.  $\times$  2 mm ID (1.83 m  $\times$  46.5 mm  $\times$  2 mm ID) and made of glass, packed with 5% SP-1200 and 1.75% Bentone 34 on 100/120 mesh Supelcoport.

#### Procedure

An experimental run to determine the concentration versus time history of an organic subjected to wet-air oxidation conditions consisted of the following events. The 1 liter reactor was filled with 700 ml of distilled water and heated to the run temperature. A measured amount of organic was then flushed into the reactor with 80 ml of heated water to start the reaction. Samples were periodically drawn and analyzed until the concentration was less than 10% of its initial value.

#### EXPERIMENTAL ANALYSIS

Typical data are shown in Figure 2. Concentrating our attention on the experimental data points, rather than the model curve which will be discussed later, it is observed that the reaction can be broken down into divided phases. At the beginning of the experiment the concentration of the organic remains approximately constant for the first hour. The scatter associated with the first two or three data points is attributed to the time required to dissolve the organic and establish phase equilibrium. This region is referred to as the induction period and is typical of free radical reactions. This is followed by a period of rapid destruction after the free radical concentration has increased to a level sufficiently high for the propagation of the reaction. The rate of change of concentration with time is approximately proportional to the organic concentration during this period. This is consistent with the behavior observed by others [1-3].

The active reaction phase is thought to be first order in both oxygen and organic concentrations, as represented by the equation

$$r = kC_2^L C_3^L \quad (1)$$

In our experiments the oxygen concentration was in great excess, allowing the use of a pseudo first-order model

$$r = k' C_2^L \quad (2)$$

for the *m*-xylene reaction.

A more detailed examination of the induction period indicates a gradual decrease in concentration with time. This

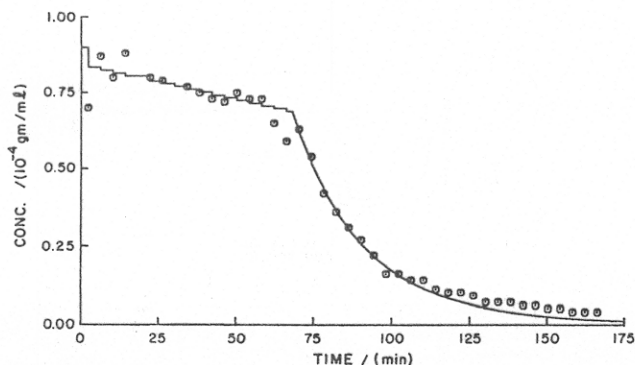


Figure 2. Comparison of experimental concentration vs. time data and model curve at 200°C and 13.8 MPa.

was found to be a function of the number of samples collected and not the time since initiation of the experiment. This indicates that the downward trend represents the re-equilibration between vapor and liquid in the reactor after a sample is withdrawn.

A preliminary experiment was made to show that the reduction in concentration during the induction period was indeed due to sampling and not reaction. Nitrogen was substituted for air, while the temperature and pressure were held at 225°C and 2500 psi (17.2 MPa). At these conditions the induction period using air would be about 30 minutes. Over a 76 minute period 18 five ml samples were taken. The liquid concentration decreased after each sample, just as it did under air pressure. Only if the stirrer was turned off did consecutive samples have the same observed concentration.

The presence of significant quantities of the organic compound in the vapor phase has received little study in previous investigations. Analysis of the concentration decrease with total liquid volume removed during the induction period allows estimation of partition coefficients between the liquid and vapor phases. By assuming that the vapor-liquid equilibrium is rapid compared to the rate of reaction during the active reaction phase, it is possible to decouple the vapor-liquid equilibrium effects from the reaction kinetics in this region. Fitting of the data to kinetic expressions without considering repartitioning between liquid and vapor can lead to significant errors in the evaluation of rate constants.

#### MODEL DEVELOPMENT

##### Henry's Law

The first step in modeling these data involves characterizing the vapor-liquid equilibrium behavior. For an organic component whose equilibrium mole fraction is close to zero, such as *m*-xylene in water, the vapor-liquid equilibrium can be approximated by

$$yP = xH \quad (3)$$

In the absence of published values for *H*, it may be estimated using induction period data during which no appreciable reaction occurs. Pressure is known, but *y* and *x* must be related to other measured variables, specifically liquid phase concentration and liquid volume. A mass balance on organic in the reactor solved for  $C_2^V$  reveals

$$C_2^V = \frac{m_2^T - V^L C_2^L}{V^T - V^L} \quad (4)$$

Thus, if the gas phase is ideal

$$y_2 = \frac{RT}{P m w_2} \left[ \frac{m_2^T - V^L C_2^L}{V^T - V^L} \right] \quad (5)$$

and for a dilute solution

$$x_2 \cong \frac{C_2^L m w_1}{\rho_1^L m w_2} \quad (6)$$

Due to density changes and the vapor pressure of water, the liquid volume is not simply the difference between the initial volume charged into the reactor and the amount removed during sampling.  $V_L$  can be computed, neglecting water's compressibility, by simultaneously solving

$$V^L = \frac{(V_0^L - V_{out}^L) \rho_0^L - m_1^V}{\rho^L} \quad (7)$$

and

$$m_1^V = \frac{P^{sat} m w_1 (V^T - V^L)}{RT} \quad (8)$$

Also,  $m_2^T$ , necessary for Equation 5, is found by

$$m_{2,k}^T = m_2^{T,0} - \sum_{i=1}^k \gamma(V_{out,i} - V_{out,i-1})C_{2,i-1}^L \quad (9)$$

Though  $H$  could be calculated from a single datum point, superior results are obtained by calculating the  $H$  associated with each point in the induction period and averaging.

#### Partitioning Mass Between Vapor and Liquid

Once an average  $H$  has been found,  $C_2^L$  can be determined at any  $m_2^T$  and  $V^L$ . The total mass of organic in the reactor is the sum of that in the liquid and that in the vapor. The mass in the vapor for an ideal gas in equilibrium with the liquid is given by

$$m_2^V = \frac{H m w_1}{RT \rho_1^L} (V^T - V^L) C_2^L \quad (10)$$

Furthermore, the mass in the liquid is

$$m_2^L = V^L C_2^L \quad (11)$$

Adding Equations 10 and 11 reveals

$$m_2^T = \left[ V^L + \frac{H m w_1}{RT \rho_1^L} (V^T - V^L) \right] C_2^L \quad (12)$$

Finally, let

$$\phi = V^L + \frac{H m w_1}{RT \rho_1^L} (V^T - V^L) \quad (13)$$

and Equation 12 becomes

$$m_2^T = \phi C_2^L \quad (14)$$

Note that  $V^L$ , and therefore  $\phi$ , is constant between reactor samples, resulting in a linear relationship between  $m_2^T$  and  $C_2^L$ . This greatly simplifies the following model.

#### Two Parameter, Two Region Model

The final task is to expand the model to include the active reaction period. An idealized plot of  $C_2^L$  versus time is shown in Figure 3. The solid line shows the actual liquid phase concentration as five samples are withdrawn. The triangles show the concentration as determined by sample analysis. Two samples were drawn in the induction period while three were drawn in the active reaction period. The rapid decrease in concentration following each sample is

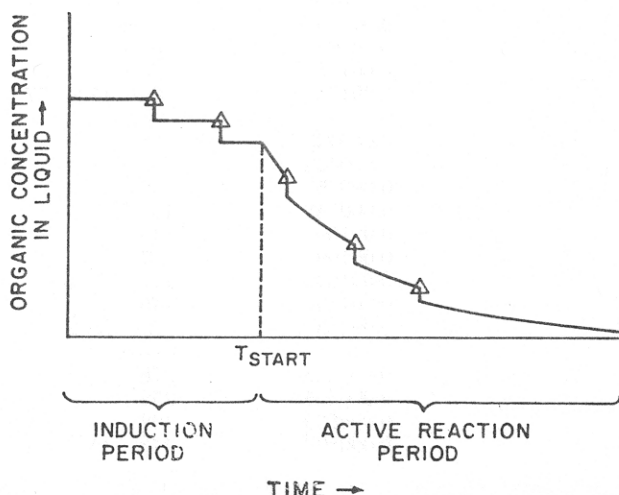


Figure 3. Idealized liquid concentration vs. time, showing the effect of sampling and reaction.

due to mass lost from the liquid to the newly created vapor space. Note, however, that though this process is rapid, it is not fast enough to decrease the sample concentration during the time it is being withdrawn (~10 seconds). This reflects an assumption about the system, namely, sampling rate  $\gg$  liquid-gas mass transfer rate  $\gg$  reaction rate. It is also assumed that there is no reaction in the vapor phase.

A general differential mass balance on organic in the reactor is

$$\frac{dm_2^T}{dt} = -q_c C_2^L - r_2 V^L \quad (15)$$

with the initial condition

$$m_2^T = m_2^0, \text{ at } t = 0$$

During the induction period the reaction term is zero, thus

$$dm_2^T = -q_c C_2^L dt \quad (16)$$

Substituting Equation 14 for  $m_2^T$ , integrating, and solving for  $C_2^L$  gives

$$C_2^L = \frac{\phi_0 - V^S}{\phi} C_{2,0}^L \quad (17)$$

Note that  $q_c$  is only non-zero during sampling and, since sampling is too fast to affect  $C_2^L$ , it is constant during integration. The integration of  $q_c dt$  is, therefore, just the sample volume. Thus, given the liquid volume before and after sampling (to compute the  $\phi$ 's), sample volume, and  $C_2^L$  before sampling, one can calculate  $C_2^L$  after the sample.

Once the induction period is over, the reaction term in Equation 15 must also be considered. First order kinetics is assumed. Substituting Equations 2 and 14 into Equation 15, and considering only the time between samples so the sample term can be ignored

$$\frac{d(\phi C_2^L)}{C_2^L} = -k' V^L dt \quad (18)$$

Since  $V^L$ , and thus  $\phi$ , is constant between samples, direct integration gives

$$C_2^L = C_{2,0}^L \exp \left[ \frac{-k' V^L}{\phi} (t - t_0) \right] \quad (19)$$

During the induction period only Equation 17 is necessary to predict the liquid phase concentration; however, once reaction starts,  $C_2^L$  is diminished continuously due to reaction (Equation 19) and discontinuously and instantaneously due to sampling (Equation 17). These equations can be combined to predict  $C_2^L$  at any time

$$C_{2,i}^L = \sum_{i=1}^m \left( \frac{\phi_{i-1} - V_i^S}{\phi_i} \right) C_{2,i-1}^L + \sum_{i=m+1,2}^n C_{2,i-1}^L \exp \left[ \frac{-k' V_{i-1}^L}{\phi_{i-1}} (t_i - t_{i-1}) \right] + \sum_{i=m+2,2}^n \left( \frac{\phi_{i-1} - V_i^S}{\phi_i} \right) C_{2,i-1}^L \quad (20)$$

with

$$t_m = t_{\text{start}} \quad (21)$$

The first summation term accounts for concentration changes due to sampling prior to the active reaction period. Thereafter, the second and third terms alternately reduce  $C_2^L$  due to reaction and due to sampling, respectively. Realize that the notation for these two terms indicates that the index is incremented by 2 rather than 1 since they represent alternating rather than simultaneous processes.

It should be stressed that the model uses only liquid phase properties, eliminating the need for a vapor phase

sampling and analysis system. This single equation provides a complete description of the concentration-time history of moderate temperature, high pressure, multi-phase batch reactor data which follow the assumptions stated in the course of the development.

## RESULTS AND DISCUSSION

The two adjustable parameters in the model are  $k'$  and  $t_{\text{start}}$ . An optimization routine, Powell's method of conjugate directions [4], was used to choose the best values of these two parameters by minimizing the sum of the square of the differences between the *m*-xylene experimental data and the model prediction. Very satisfactory results were obtained, as can be seen by comparing the calculated line and the experimental data in Figure 2. For this particular run the first six data points after the active reaction began were used for the fit.

The traditional method of determining first order rate constants is from the slope of a semi-log plot of  $C/C_0$  versus time. Results from this method are compared with our model results in Table 1. The pseudo first-order rate constants determined by the traditional method are low by a factor of 1.5 to 2.5. This discrepancy is due to the fact that the traditional method fails to realize that, as the *m*-xylene reacts in the liquid phase, it is being replenished from the vapor phase. The reaction is proceeding much faster than the data indicate upon casual inspection. Mathematically

this is explained by inspecting Equation 19. This is just the familiar integrated form of the first-order rate expression, but with the exponential term multiplied by the ratio  $V^L/\phi$ . If  $V^L$  does not change much during the rapid reaction period, an average value for this ratio can be used during this period. The quotient of the  $k''$  values in Table 1 and the average value of  $V^L/\phi$  very closely approximates the  $k'$  obtained from the Equation-20 model. This suggests a quick, easy-to-use method for estimating  $k'$  in the absence of time and/or a computer.

A more extensive compilation of results is found in Table 2. The *m*-xylene Henry's law constants reported here were calculated as outlined earlier. Though certainly within the same order of magnitude, there is excessive scatter in these values. Highly dependent on  $m_2^0$ , most of this discrepancy is attributed to difficulties associated with injecting a precise amount of *m*-xylene into a high pressure system. An order of magnitude study, however, reveals that this uncertainty will only minimally affect  $k'$ . The values of  $k'$  reported in Table 2 are converted to intrinsic rate constants using dissolved oxygen concentrations determined from Himmelblau [5]. The intrinsic rate constants were used to construct an Arrhenius plot (Figure 4) from which an activation energy of 12.1 kcal/mol (50.7 kJ/mole) was determined for the wet-air oxidation of *m*-xylene. 95% confidence limits are shown on the figure. At 200°C and 240°C only four data points are available, resulting in large confidence limits.

From this work it is obvious that significant errors in estimating the reaction rate can be caused by neglecting the effects of vapor-liquid equilibrium on batch reactor data. Excellent results were obtained using the model presented in this paper to predict the liquid phase concentration of a sparingly soluble, volatile hydrocarbon subjected to wet-air oxidation conditions.

TABLE 1. COMPARISON OF RATE CONSTANT CALCULATION METHODS

Run No.	Pseudo first-order rate constant from vapor-liquid equilibrium model, Equation 20 $k'/(l/min)$	Pseudo first-order rate constant from slope of log concentration vs. time data $k''/(l/min)$
XYL-830928-1	0.0840	0.0442
XYL-830929-1	0.0962	0.0364
XYL-831003-1	0.0960	0.0391
XYL-831004-1	0.0809	0.0327
XYL-831005-1	0.141	0.0964
XYL-831010-2	0.187	0.112
XYL-831006-1	0.208	0.146
XYL-831010-1	0.185	0.135

## NOMENCLATURE

### English symbols

- $C$  = Concentration (mass volume<sup>-1</sup>)
- $H$  = Henry's law constant (pressure<sup>-1</sup>)
- $k$  = Intrinsic rate constant (volume mass<sup>-1</sup> time<sup>-1</sup>)
- $k'$  = Pseudo first-order rate constant (time<sup>-1</sup>)
- $k''$  = Pseudo first-order rate constant obtained from the "traditional method" (time<sup>-1</sup>)
- $m$  = Mass

TABLE 2. WET-AIR OXIDATION OF *m*-XYLENE: EXPERIMENTAL CONDITIONS AND MODEL RESULTS

$T/^\circ\text{C}$	$P/\text{psi}^*$	Henry's Law Constant $H/\text{psi}^{-1**}$	Pseudo First-Order Rate Constant $k'/(l/min)$	Dissolved Oxygen Concentration $C_2/(gm/ml)$	Intrinsic Rate Constant $k/(ml/gm\ min)$
200	2000	79100	0.0840	0.00103	81.6
200	2000	59100	0.0962	0.00103	93.4
200	2500	112400	0.0960	0.00132	72.7
200	2500	78000	0.0809	0.00132	62.3 AVE=77.3
225	1000	76400	0.0788	0.000423	186
225	1000	53200	0.0676	0.000423	160
225	1500	81100	0.101	0.000758	133
225	1500	122100	0.0888	0.000758	117
225	2000	76200	0.141	0.00109	129
225	2000	92900	0.187	0.00109	172
225	2000	123400	0.124	0.00109	114
225	2500	77200	0.208	0.00143	145
225	2500	68700	0.185	0.00143	129 AVE=143
240	1000	119600	0.118	0.000425	278
240	1000	115800	0.107	0.000425	252
240	1500	166200	0.161	0.000839	192
240	1500	89600	0.124	0.000839	148 AVE=218

\*to convert to MPa multiply by 6895

\*\*to convert to MPa<sup>-1</sup> multiply by  $1.450 \times 10^{-4}$

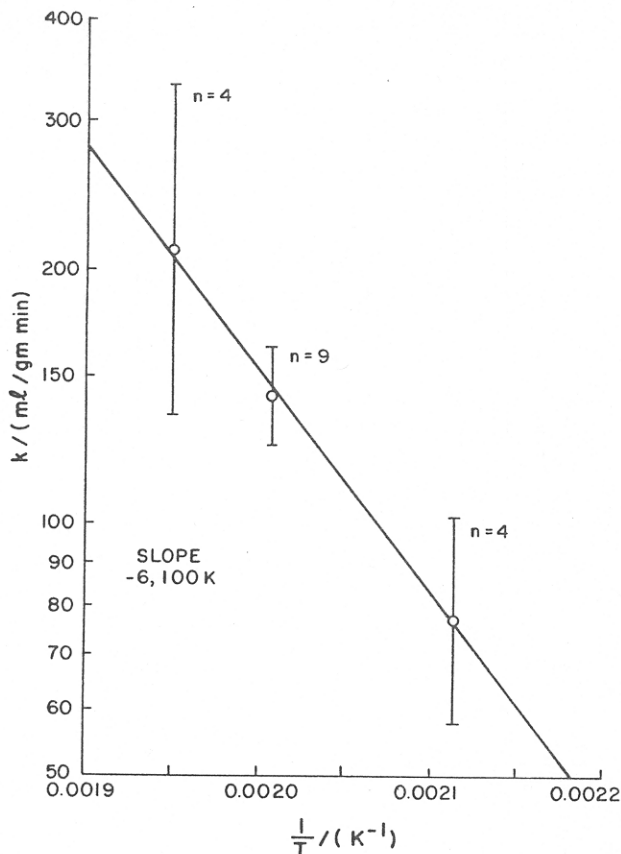


Figure 4. Arrhenius plot.

- $mw$  = Molecular weight (mass mole<sup>-1</sup>)  
 $P$  = Pressure  
 $q$  = Flowrate (volume time<sup>-1</sup>)  
 $r$  = Reaction rate (mass volume<sup>-1</sup> time<sup>-1</sup>)  
 $R$  = Universal gas constant (energy mole<sup>-1</sup> temperature<sup>-1</sup>)  
 $t$  = Time  
 $T$  = Temperature  
 $V$  = Volume  
 $x$  = Liquid phase mole fraction  
 $y$  = Gas phase mole fraction

#### Greek symbols

- $\gamma$  =  $\rho_0^l/\rho^l$   
 $\rho$  = Density (mass volume<sup>-1</sup>)  
 $\phi$  = Defined in Equation 13

#### Subscripts

- $0$  = At initial conditions  
 $1$  = Water  
 $2$  = Organic (*m*-xylene)  
 $3$  = Oxygen  
 $e$  = Exit  
 $out$  = Cumulative volume removed from the system  
 $start$  = Beginning of reaction period

#### Superscripts

- $0$  = At initial conditions  
 $L$  = Liquid phase  
 $S$  = Sample  
 $sat$  = At saturation conditions  
 $T$  = Total, liquid and vapor phase  
 $V$  = Vapor phase

#### Indices

- $i$  = Summation index  
 $k$  = Total number of points  
 $m$  = Last value before active reaction period  
 $n$  = 2 (total points) -  $m$

#### ACKNOWLEDGEMENT

This project has been supported with Federal funds from the U.S. Environmental Protection Agency under Contract 68-03-3014. The content of this paper has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the official views or policies of the U.S. Environmental Protection Agency. Mention of trade names, commercial products, or organizations does not constitute endorsement or recommendation for use by the U.S. government, Rockwell International, or Louisiana State University.

#### LITERATURE CITED

- Day, D. C., R. R. Hudgins, and P. L. Silveston, "Oxidation of Propionic Acid Solutions," *Can. J. of Chem. Engr.* **51**, 733 (1973).
- Shibaeva, L. V., D. I. Metelitsa, and E. T. Denisov, "Oxidation of Phenol with Molecular Oxygen in Aqueous Solutions: I. The Kinetics of the Oxidation of Phenol with Oxygen," *Kinetics & Catalysis* **10**(5), 832 (1969).
- Skaates, J. M., B. A. Briggs, R. A. Lamparter, and C. R. Bailod, "Wet Oxidation of Glucose," *Can. J. of Chem. Eng.* **59**, 517 (1981).
- Powell, M. J. D., "An Effective Method of Finding the Minimum of Several Variables Without Calculating Derivatives," *Computer J.* **7**, 155 (1964).
- Himmelblau, D. M., "Solubility of Inert Gases in Water," *J. of Chem. and Eng. Data* **5**(1), 10 (1960).



R. Scott Willms is a graduate student in the Department of Chemical Engineering at Louisiana State University.



Anne M. Balinsky is a graduate student in the Department of Chemical Engineering at Louisiana State University.



Danny D. Reible is Assistant Professor of Chemical Engineering at Louisiana State University. He holds a Ph.D. in chemical engineering from the California Institute of Technology.



David M. Wetzel is Associate Professor of Chemical Engineering at Louisiana State University. He holds a Ph.D. in chemical engineering from the University of Delaware.



Douglas P. Harrison is Professor of Chemical Engineering at Louisiana State University. He holds a Ph.D. in chemical engineering from the University of Texas, Austin.