



LOW TEMPERATURE AQUEOUS PHASE CATALYTIC OXIDATION OF PHENOL

James E. Atwater*, James R. Akse, Jeffrey A. McKinnis, and John O. Thompson

UMPQUA Research Company,
P.O. Box 609, Myrtle Creek, Oregon 97457.

(Received in USA 25 April 1996; accepted 31 October 1996)

Abstract. Low temperature aqueous phase heterogeneous catalytic oxidation of dissolved organic compounds is a potential means for remediation of contaminated ground and surface waters, industrial effluents, and other wastewater streams. The capability for operation at substantially milder conditions of temperature and pressure, in comparison to those required for supercritical water oxidation and closely related wet air oxidation processes, is made possible through the use of an extremely active bi-metallic noble metal catalyst. Phenol degradation studies were conducted using continuous flow packed bed microreactors configured to minimize the deviation from plug flow. Reaction rate constants for the disappearance of phenol were determined using a pseudo first order plug flow kinetic model over the temperature range between 35–65°C. These data were used to derive Arrhenius activation energies and pre-exponential factors. Reactor operating conditions required for mineralization of phenol have been determined. Copyright © 1996 Elsevier Science Ltd

Key words: catalyst, heterogeneous, oxidation, aqueous, phenol, low temperature.

INTRODUCTION

Low temperature aqueous phase heterogeneous catalytic oxidation is a promising technique for the destruction of organic water pollutants. While a great many advanced oxidation processes have been reported which utilize hydrogen peroxide and ozone, separately or in combination, relatively few practical environmental remediation methodologies require only oxygen. The use of molecular oxygen for the oxidation of a variety of aqueous organic contaminants under supercritical conditions has received considerable attention¹. The somewhat milder wet air oxidation process which, in general, requires only slightly less rigorous conditions of temperature and pressure has also been demonstrated for the oxidation of dissolved organics using both elemental oxygen and air as the oxidant². Both techniques are limited in their applicability to the treatment of contaminated waters on a practical scale owing to energy requirements, the cost of equipment needed for high pressure operation, and safety considerations. Other problems with these techniques include the incomplete oxidation of some contaminants leading to the formation of organic acids, and the production of additional contaminants through pyrolysis and isomerization reactions, such as the formation of dioxins from chlorinated phenolic precursors³.

* To whom correspondence should be addressed: e_mail: atwaterj@ccmail.orst.edu

Other than investigation of photocatalytic methods, very little work has been done toward the development of low temperature heterogeneous catalysis for the oxidation of toxic or otherwise unwanted organic contaminants in aqueous systems. Sadana and Katzer studied the aqueous phase catalytic oxidation of 4 - 11 g-L⁻¹ concentrations of phenol over a 10% copper oxide on γ -alumina catalyst in the temperature range between 100 - 220°C, and pressures between 1 - 17 atmospheres (atm) using a batch reactor⁴. At 1 atm, reaction rates were limited by O₂ solubility. At elevated pressures higher conversions were obtained. At 145°C and 17 atm, 90% oxidation was observed. Complete mineralization was not reported, but significant quantities of CO₂ were detected. At these relatively high contaminant concentrations, oxygen limitations due to solubility were a problem, even at 17 atm. Levec reported the aqueous phase oxidation of phenol, 4-nitrophenol, 2-chlorophenol, and t-butyl alcohol in concentrations ranging between 2 - 5 g-L⁻¹, over a catalyst consisting of 42% by weight copper oxide, 47% zinc oxide, and 10% alumina^{5,6}. In this work, a batch reactor operating at 130°C and 6 atm, and continuously sparged with oxygen was charged with aqueous contaminants. Contaminant concentrations were monitored versus time. By 100 minutes, concentrations of phenol, chlorophenol, and butyl alcohol approached zero. Nitrophenol proved more difficult to oxidize, with roughly 1/3 of the original concentration remaining after 100 minutes.

Workers in our laboratory have demonstrated the deep oxidation (mineralization) of several classes of organic contaminant in the aqueous phase using oxygen over noble metal catalysts at temperatures between 120 - 160°C, and pressures between 2.3-5.1 atm⁷. This work focused on the development of catalytic oxidation as a unit process of water reclamation technology for spacecraft regenerative life support systems. Contaminants studied have been those typical of humidity condensates, urine distillates, and wastewaters arising from personal hygiene. The organic compounds occurring in highest quantity in these contaminated waters are low molecular weight alcohols, carboxylic acids, urea, and soaps. The experimental results have indicated deep oxidation (mineralization) of single component and mixed contaminant streams containing dissolved organics at levels between 10 - 200 mg-L⁻¹ using a platinum-ruthenium bi-metallic noble metal catalyst on a high surface area activated carbon support (Pt-Ru/C) in a continuous flow reactor operating at 121-125°C, and 3 - 6 atm⁸⁻¹¹. More recently, the performance of this system in the degradation of trichloroethylene (TCE), a significant groundwater contaminant, has been demonstrated¹². Deep oxidation of TCE was observed at 90°C. In the current work, initial results in the evaluation of the efficacy of this catalyst for use in the decomposition of aqueous phenol are reported. The conditions required for mineralization are identified and pseudo-first order kinetics for the disappearance of phenol from aqueous solution are reported.

EXPERIMENTAL SECTION

Materials. Phenol and potassium ferricyanide were purchased from Mallinckrodt (Chesterfield, MO). 4-aminoantipyrine was acquired from J.T. Baker (Phillipsburg, NJ). 1 M Ω deionized (DI) water was prepared using mixed ion exchange beds and carbon adsorption (Culligan). Breathing quality compressed oxygen was purchased from Pacific Airgas (Portland, OR). The platinum-ruthenium bimetallic catalyst (Pt-Ru/C) was prepared on an activated carbon support by direct impregnation of the substrate using ruthenium(III) chloride dissolved in 15% HCl, followed by impregnation of platinum using aqueous hexachloroplatinic acid. Metallic loadings of 5% ruthenium and 20% platinum (w/w) were obtained. The catalyst preparation methodology has been described in greater detail elsewhere¹².

Analytical Instruments and Methods. The 4-aminoantipyrine spectrophotometric method was used to determine phenol concentrations. Absorbance at 500 nm was measured using a Hewlett-Packard 8452A diode array UV-

visible spectrophotometer¹³. Total organic carbon (TOC) was determined using both ASTRO 2001 and Beckman 915 TIC/TOC analyzers.

Oxygen Saturators. Two O₂ saturation modules were assembled, each consisting of a bundle of hollow fiber non-porous polydimethylsiloxane membranes in a tube-in-shell arrangement. The first O₂ saturator consisted of a bundle of 114 fibers inside a cylindrical polyvinylchloride shell, 26.7 cm in length and 2.54 cm in diameter with a fiber internal volume of 2.3 cm³ and an active area of 251 m². The second O₂ saturator consisted of 300 fibers inside a polycarbonate shell inserted into a 316 stainless steel housing. Dimensions of the shell were 26.7 cm in length and 2.54 cm in diameter. The hollow fiber internal volume and surface area were 4.1 cm³ and 448 cm² respectively. In both cases, the gas outlet to the shell was dead-ended. The hollow fibers were attached to manifolds at the inlet and outlet faces by an epoxy potting compound.

The oxygenation modules were designed to equilibrate the gas phase in the shell with an aqueous stream flowing through the hollow fibers¹⁴. At equilibrium, the relationship between the partial pressure of O₂ and the dissolved aqueous O₂ concentration is described by Henry's Law

$$h = \frac{pO_2}{x} \quad (1)$$

The value of h as a function of absolute temperature (°K) is given by Benson *et al.*¹⁵ as,

$$\ln h = 3.71814 + 5596.17 \text{ } ^\circ\text{K}^{-1} - 1049668 \text{ } ^\circ\text{K}^{-2} \quad (2)$$

In operation, constant O₂ pressure is applied to the shell of the saturator. Oxygen diffuses through the semipermeable membranes and into the flowing aqueous stream inside the fibers and equilibrates according to the relationships expressed by (1) and (2). This oxygenated stream is then fed to the inlet of the catalytic oxidation reactor.

Low Temperature Aqueous Phase Catalytic Oxidation Reactor. Two bench-top catalytic oxidation test-beds, consisting of temperature control and reactor sub-systems, were assembled. One was used for kinetic studies, and the other was employed in the mineralization experiments. A schematic of the apparatus is shown in Figure 1. The temperature control unit was comprised of silicon oil bath, coiled heating element (Watlow), mixer, and Omega Series CN 1200 temperature controller. A type K thermocouple submerged in the oil bath provided temperature input to the controller which regulated power to the heating element. This control scheme maintained oil bath temperatures within $\pm 0.5^\circ\text{C}$. A second thermocouple was located at the outflow end of the catalytic reactor. The reactor unit consisted of a packed catalyst bed, oxygen saturator, influent preheating coil, effluent cooling coil, pressure relief valve, Eldex A-30-VS metering pump, and Nupro model SS-RL354 back-pressure regulator. The preheating and cooling coils were prepared using 6.1 meter lengths of 316 stainless steel tubing with an internal diameter of 0.318 cm and 0.09 cm wall thickness. The 5 cm³ packed catalyst beds were configured as plug flow tubular microreactors, confined within 1.27 cm diameter x 0.09 cm wall thickness 316 stainless steel housings. The second test-bed differed from the above by the use of a magnetic hot plate-stirrer as the heat source and a cooling water coil inside the oil bath to control temperature, and by the use of a Masterflex model 7520-35 multichannel peristaltic pump. The second system was configured with an 18 cm³ catalyst bed and was used in the mineralization

studies. Small catalyst beds were used in the kinetics experiments to facilitate incomplete decomposition of phenol. This larger bed was used to explore the mineralization of phenol under milder conditions.

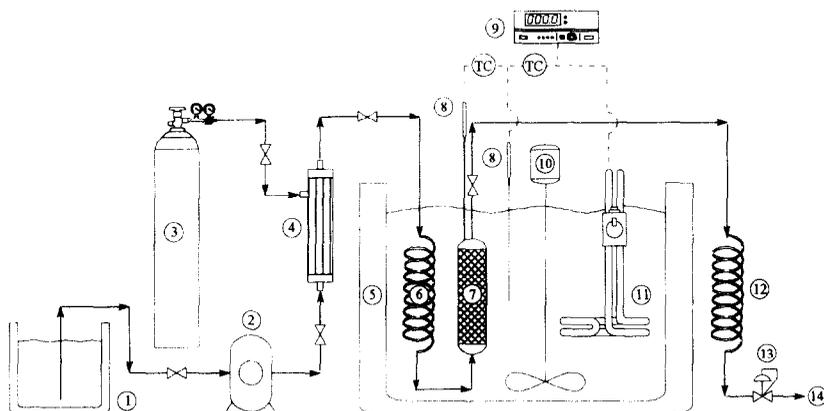


Figure 1. Aqueous Phase Catalytic Oxidation Test-bed: 1) Influent Reservoir, 2) HPLC Pump, 3) O₂, 4) O₂ Saturator, 5) Oil Bath, 6) Preheating Coil, 7) Catalytic Microreactor, 8) Thermo-couple, 9) Temperature Controller, 10) Mixer, 11) Heating Element, 12) Cooling Coil, 13) Back-Pressure Regulator, 14) Outlet.

To keep O₂ in solution and maintain single phase liquid flow, the reactor was pressurized. The two contributing factors to reactor pressure were operating temperature and the required level of O₂ saturation. The pressure required to overcome head loss in the plumbing and across the catalyst bed was small in comparison. In operation, sufficient pressure was applied to the shell side of the O₂ saturator to achieve the desired dissolved O₂ concentration in the reactor influent. The oxygen saturated stream then passed through the heating coil which brought it to the specified reactor operating temperature. The contaminant laden aqueous stream then flowed into the packed catalyst bed where the oxidation reactions were initiated. The reactor outflow passed through the cooling coil where heat was dissipated by forced air convection. The cooling coil produced an ambient temperature effluent. The back-pressure regulator maintained reactor operating pressure.

RESULTS AND DISCUSSION

Because of the complexity of the mechanism involved in the mineralization of phenol and the convenience of the spectrophotometric methodology for the quantitation of phenol in aqueous media, the initial kinetics experiments were based solely upon the rate of disappearance of phenol. No attempt was made to characterize the series of steps required for complete decomposition into inorganic reaction products. Likewise, the pseudo-first order kinetic model was adopted for experimental convenience. No attempt was made to determine true reaction order. These simplifications, however, provided the basis for a rapid estimation of the effects of space velocity and temperature on phenol degradation rates using the bi-metallic catalyst, and for the determination of nominal conditions required to achieve complete mineralization of phenol in aqueous solution.

Plug Flow Conditions. Initial work was conducted to determine appropriate reactor dimensions to minimize deviation from the plug flow ideal state^{16,17}. This condition imposes constraints on superficial fluid velocity, and the ratio of bed length to catalyst particle diameter. The deviation from plug flow is not significant if,

$$N_{Pe} > 8n \ln \left(\frac{1}{1-x} \right) \quad (3)$$

The Peclet number (N_{Pe}) is calculated as

$$N_{Pe} = 0.034 \left(\frac{v D_p \rho}{\mu} \right)^{0.53} \left(\frac{L}{D_p} \right) \quad (4)$$

The L/D_p constraint can be summarized as

$$\frac{L}{D_p} > 235.3 \left(\frac{v D_p \rho}{\mu} \right)^{-0.53} \left[n \ln \left(\frac{1}{1-x} \right) \right] \quad (5)$$

For the reactors used in this study, a worst case L/D_p ratio of ≈ 30 was calculated for a 5 cm³ microreactor using the largest diameter of the catalyst particle size distribution. The right hand side of equation (5) was evaluated using a typical fractional void volume of 0.28 over the range of temperatures, flow rates, reactant concentrations, and conversions used to derive rate constants. In all cases the relation expressed in (5) was obeyed, indicating that the experiments were performed under conditions which, to a first approximation, can be considered as plug flow.

Phenol Degradation Kinetics. Reaction kinetics were studied using constant aqueous phenol influent concentrations under conditions of varying flow rates and temperatures. At each temperature, reactor effluent phenol concentrations were determined for each flow rate. Reactor space-times were determined as

$$\tau = \frac{V_r \phi}{Q} \quad (6)$$

Rate constants to the first order plug flow rate law were derived from the resulting concentration versus space-time ordered pairs, (C , τ), using the Levenberg-Marquardt method¹⁸. Correlation coefficients (r^2) for the derived rate constants were calculated using a linear regression of experimentally observed phenol concentrations versus those calculated from the first order rate law. At least four data points were gathered for each temperature of operation. Kinetics experiments were conducted at four temperatures between 35-65°C. Rate constants as functions of temperature were fitted to the Arrhenius equation as ($1/T$, $\ln k$) ordered pairs using a least squares approximation to determine the activation energy and pre-exponential factor.

Pseudo-first order rate constants were determined for phenol disappearance at 35°C, 45°C, 55°C, and 65°C using two 4.8 cm³ tubular microreactors and an influent containing 0.16 mM (15 mg-L⁻¹) phenol dissolved in DI water, with an oxygen saturation of 2.95 mM (94.5 mg-L⁻¹). The fractional void volume for the packed catalyst bed was 0.28. Decay curves for the experiments conducted at 35°C and 65°C are shown in Figures 2 and 3, respectively. The derived rate constants and correlation coefficients are summarized in Table I. These data were used to determine an Arrhenius activation energy of 33.8 kJ-mol⁻¹, and a pre-exponential factor of 6.17x10⁴ s⁻¹ for

the reaction, with $r^2 = 0.9925$. The Arrhenius relationship for the reaction rate constant as a function of temperature is shown in Figure 4.

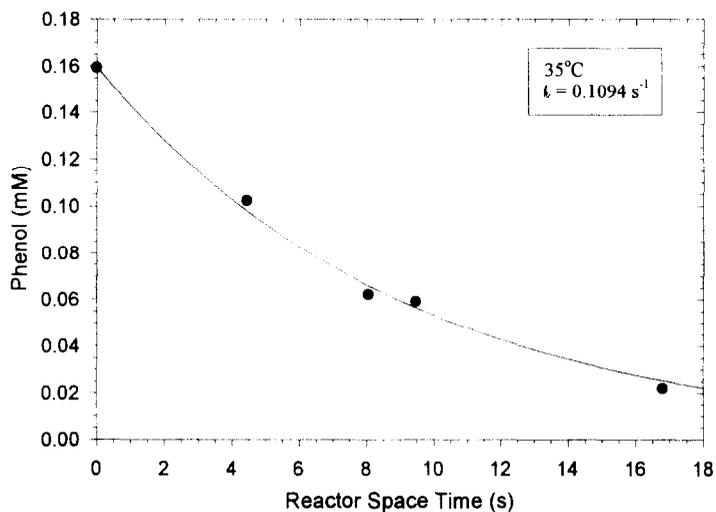


Figure 2. Pseudo-First Order Kinetics - Phenol Oxidation at 35°C.

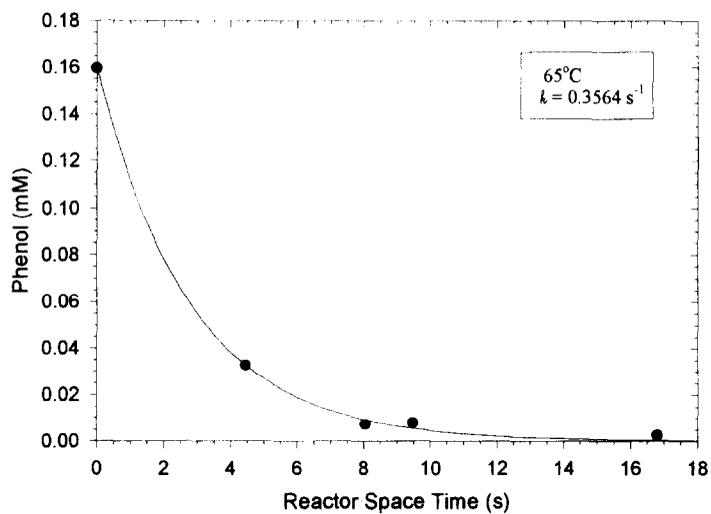
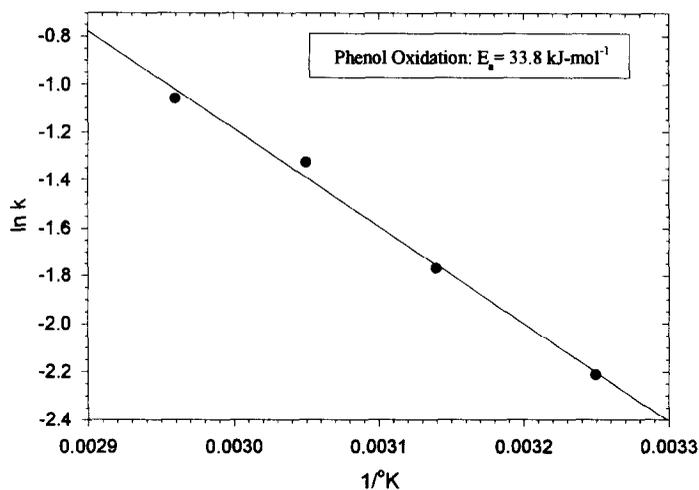


Figure 3. Pseudo-First Order Kinetics - Phenol Oxidation at 65°C.

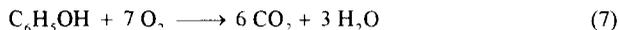
Table I. Pseudo-First Order Phenol Degradation Kinetics

Temperature (°C)	Rate Constant (s ⁻¹)	Correlation Coefficient (r ²)
35	0.1094	0.9956
45	0.1703	0.9952
55	0.2658	0.9898
65	0.3564	0.9994

**Figure 4.** Arrhenius Plot for Phenol Degradation.

A distinctive feature of the kinetics experiments for phenol decomposition was the lengthy time period required for steady state reactor operation to be achieved. This was due to the high surface area and temperature dependent sorption capacity of the activated carbon catalyst support ($\approx 1800 \text{ m}^2\text{-g}^{-1}$). When flow was first established at the initial temperature of operation the reactor effluent contained no contaminant. This situation arose from the combined effects of sorption and oxidation. If the temperature was insufficient to promote complete mineralization of the contaminant, the reactor effluent concentration slowly rose to a steady state level. If the temperature was lowered, the reactor effluent concentration fell due to the increased sorption capacity of the catalyst bed. As sorption equilibrium at the lower temperature was approached, the reactor output rose again to a new steady state value. When reactor temperature was increased, effluent contaminant levels rose (due to desorption), and then fell until a new steady state was reached. Reaction rates were determined only after steady state conditions were evident.

Mineralization of Phenol. The overall reaction for the complete oxidation of phenol to inorganic products is



Conditions required for the mineralization of aqueous phenol were investigated using an 18 cm³ tubular microreactor with 0.28 fractional void volume. The larger reactor volume was used because we wished to explore the complete destruction of phenol under lower temperature conditions which required operation at longer space-times. This was easier to achieve using a larger bed size, rather than using lower flow rates. The 18 cm³ reactor was operated at a flow rate of 1.00 cm³-min⁻¹, corresponding to a space-time of 5.04 minutes and a space velocity of 11.9 h⁻¹. The reactor was challenged with an influent aqueous phenol concentration of 15 mg-L⁻¹ (9.01 mg-L⁻¹ as C). Initial estimates of reactor operating temperature and flow rate required for mineralization of phenol were based upon the outcome of the kinetics experiments. Reactor temperature was adjusted in 10°C increments and effluent total organic carbon (TOC) levels were determined after attainment of steady state operation until TOC values of below the lower limit of detection for the analyzer resulted (<0.2 mg-L⁻¹). The results indicated deep oxidation (mineralization) of phenol at 60°C

CONCLUSIONS

Low temperature aqueous phase heterogeneous catalytic oxidation using molecular oxygen and the bi-metallic Pt-Ru/C catalyst has been shown to completely convert phenol into inorganic constituents at the relatively mild temperature of 60°C. This is the lowest temperature reported to date for any heterogeneous catalytic oxidative process for wastewater treatment excluding photocatalytic methods. Reaction rate constants have been determined for phenol disappearance using the pseudo-first order plug flow kinetic model over a range of temperatures. Under conditions of O₂ excess, first order kinetics were found to describe the catalytic oxidation reactions of phenol with reasonable accuracy. Arrhenius activation energies and pre-exponential factors have been determined. The relatively low value for the activation energy suggests that global reaction rates may be pore diffusion limited. This is not surprising given the extremely high surface area of the catalyst support. No indication of catalyst inactivation or degradation was evident, although further experimentation will be required to examine this phenomenon.

The experimental results indicate the viability of low temperature aqueous phase heterogeneous catalytic oxidation, using the bi-metallic catalyst, as a potential means of environmental remediation. Further work will be required to assess the amenability of other important aqueous organic contaminants to this novel water treatment methodology. In conjunction with this work, the relative importance of adsorption and limitations in surface reaction rate, film diffusion and pore diffusion must also be determined for a range of potential reactants²⁰⁻²².

ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation under award number DMI 9460162.

Nomenclature

- C = concentration, mM
- D_p = catalyst particle diameter
- E_a = Arrhenius activation energy, kJ-mol⁻¹
- h = Henry's Law constant, atm

- k = reaction rate constant, s^{-1}
 L = catalyst bed length, cm
 n = moles of reactant
 N_{pe} = Peclet number
 pO_2 = atmospheric O_2 partial pressure, atm
 ρ = density, $g\text{-cm}^{-3}$
 ϕ = fractional void volume
 Q = flow rate, $cm^3\text{-min}^{-1}$
 r^2 = statistical correlation coefficient
 T = temperature, $^{\circ}K$
 τ - reactor space-time, min
 μ = viscosity, Pa-s
 v = fluid velocity, $cm\text{-s}^{-1}$
 V_r = reactor volume, cm^3
 χ = dissolved O_2 mole fraction
 x = fractional reactant consumed

REFERENCES

1. Tester, J.W.; Holgate, H.R.; Armellini, F.J.; Webley, P.A.; Killilea, W.R.; Hong, G.T.; Barner, H.E. Supercritical Water Oxidation Technology. Process Development and Fundamental Research, in *Emerging Technologies in Hazardous Waste Management III*; Tedder, W.D.; Pohland, F.G., Eds., American Chemical Society: Washington, D.C., 1993
2. Mishra, V.S.; Mahajani, V.V.; Joshi, J.B.; Wet Air Oxidation. *Ind.Eng.Chem.Res.* 1995, **34**, 2.
3. Thornton, T.D.; LaDue, D.E.,III; Savage, P.E.; Phenol Oxidation in Supercritical Water: Formation of Dibenzofuran, Dibenzo-p-dioxin, and Related Compounds. *Environ. Sci. Technol.* 1991, **25**, 1507.
4. Sadana, A. and Katzer, J.R.; Catalytic Oxidation of Phenol in Aqueous Solution over Copper Oxide. *Ind. Eng. Chem., Fundam.* 1974, **13**, 127.
5. Levec, J.; Catalytic Oxidation of Toxic Organics in Aqueous Solution. *Appl. Catal.* 1990, **63**, L1.
6. Levec, J.; German Patent Application P 39 38 835.2, November, 1989.
7. Akse, J.R. and Jolly, C.D.; Catalytic Oxidation for Treatment of ECLSS & PMMS Waste Streams; SAE Technical Paper Series No. 911539, in *Regenerative Life Support Systems & Processes*; SP-873, SAE, Warrendale, PA, 1991
8. Akse, J.R.; Thompson, J.; Scott, B.; Jolly, C.D.; Carter, D.L.; Catalytic Oxidation for Treatment of ECLSS & PMMS Waste Streams. *SAE Trans., J. Aerosp.* 1992, **101**, 910.
9. Akse, J.R. and Atwater, J.E.; Advanced Catalytic Methods for the Destruction of Environmental Contaminants; Paper No. 95-LS-70, presented at AIAA Life Sciences and Space Medicine Conference '95, Houston, April 3-5, 1995.
10. Akse, J.R.; Atwater, J.E.; Thompson, J.O.; Wheeler, R.R., Jr.; A Breadboard Electrochemical Water Recovery System for Producing Potable Water from Composite Wastewater Generated in Enclosed Habitats, in *Water*

- Purification by Photocatalytic, Photochemical, and Electrochemical Processes*; Rose, T.L.; Conway, B.E.; Murphy, O.J.; Rudd, E.J, Eds., Electrochemical Society, 1994.
11. Akse, J.R.; Atwater, J.E.; Schussel, L.J.; Verostko, C.E. Development and Fabrication of a Breadboard Electrochemical Water Recovery System. *SAE Trans., J. Aerosp.* 1993, **102**, 513.
 12. Atwater, J.E.; Akse, J.R.; McKinnis, J.A.; and Thompson, J.O.; Aqueous Phase Heterogeneous Catalytic Oxidation of Trichloroethylene. *Appl. Catal. B.*, accepted June 1996.
 13. Greenberg, A.E.; Trussel, A.E.; Clesceri, L.S., (Eds.); *Standard Methods for the Examination of Water and Wastewater*; 16th Ed., APHA: Washington, D.C., 1985.
 14. Ming-Chien, Y.; Cussler, E.L.; Designing Hollow Fiber Contactors. *AIChE J.* 1986, **32**, 1910.
 15. Benson, B.B.; Krause, D., Jr.; Peterson, M.A.; The Solubility and Isotopic Fractionation of Gases in Dilute Aqueous Solution. I. Oxygen. *J. Solution Chem.* 1979, **8**, 655.
 16. Dautzenberg, F.M.; Ten Guidelines for Catalyst Testing, in *Characterization and Catalyst Development: An Interactive Approach*; ACS Symposium Series 411, American Chemical Society: Washington, D.C., 1989.
 17. Silverstein, J.; Shinnar, R.; Design of Fixed Bed Catalytic Microreactors. *Ind. Eng. Chem., Process Des. Develop.* 1974, **14**, 127.
 18. Press, W.H.; Flannery, B.P.; Teukolsky, S.A.; Vetterling, W.T.; *Numerical Recipes: The Art of Scientific Computing*; Cambridge: New York, 1986.
 19. Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K.; *The Properties of Gases and Liquids*; 3rd Ed., McGraw-Hill: New York, 1977.
 20. Hougen, O.A.; Watson, K.M.; *Chemical Process Principles, Part 3, Kinetics and Catalysis*; Wiley: New York, 1947.
 21. Kittrell, J.R.; Mezaki, R. Discrimination Among Rival Hougen-Watson Models Through Intrinsic Parameters. *AIChE J.* **1967**, **13**, 389.
 22. Levenspiel, O. *Chemical Reaction Engineering*; 2nd Ed., Wiley: New York, 1972.