

Enhanced Wet Air Oxidation: Synergistic Rate Acceleration upon Effluent Recirculation

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Wet air oxidation (WAO) reactions of cellobiose, phenol, and syringic acid were carried out under mild conditions (155 °C; 0.93 MPa O₂; soluble catalyst, Na₂[PV₂Mo₁₀O₄₀]). Initial oxidation rates were rapid but decreased to small values as less reactive oxidation products accumulated. Recalcitrant oxidation products were consumed more rapidly, however, if additional cellobiose or phenol was added, a procedure equivalent to recirculation of WAO-reactor effluent. A half-fraction, factorial investigation was used to correlate rate enhancement with individual experimental variables: using a two-level design, effluents from the WAO of cellobiose were combined with unreacted cellobiose and WAO resumed. The effluents were degraded more rapidly than could be accounted for by residence time alone. Correlations identified by the factorial investigation were consistent with oxidation of recalcitrant compounds by highly reactive intermediates generated during the initially rapid radical-chain autoxidation of unreacted cellobiose.

Introduction

Wet air oxidation (WAO)—high-temperature reaction with oxygen in water—is used to degrade organic compounds present at low concentrations. To accomplish this, aqueous organic-waste streams too dilute to be incinerated economically, or too concentrated or toxic to be treated biologically, are reacted with oxygen (1–20 MPa O₂) at temperatures from 100 to 350 °C.¹ Optimally, the dissolved organic compounds would be oxidized to carbon dioxide and water. Usually, however, the compounds initially present are partially oxidized to less reactive derivatives, usually low-molecular-weight organic acids.² As the compounds initially present are depleted and the recalcitrant products of their partial oxidation accumulate, the rate of wet oxidation decreases dramatically: the apparent rate constant decreases by an order of magnitude or more. This decrease in rate limits the usefulness and economic viability of WAO processes.

Numerous methods for increasing the rate and effectiveness of WAO processes have been reported. Homogeneous catalysts, most notably Cu(II) salts,^{2,3} increase the overall reaction rate and catalyze the oxidation of low-molecular-weight organic acids. While ranging in effectiveness and longevity, heterogeneous catalysts^{1b-d} such as CuO and ZnO on alumina⁴ or Ru, Pd, or Pt on metal-oxide supports^{1d,5} or on more acid-resistant supports such as activated carbon⁶ or graphite^{6a} have the advantage of being more readily recovered than homogeneous catalysts. Additional chemical and physical-chemical modifications, such as the use of ozone,^{2f,7} hydrogen peroxide⁸ photocatalysis,⁹ ultra-

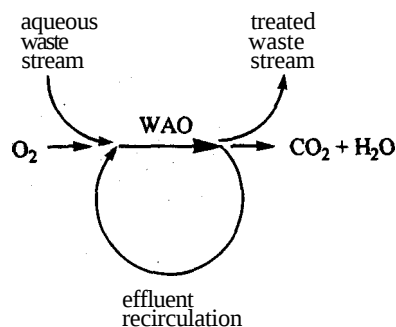


Figure 1. Proposed process schematic for synergistically enhanced wet air oxidation (WAO).

sound,¹⁰ and supercritical water,¹¹ have also been reported.

These efforts aim to minimize the accumulation of recalcitrant organic compounds by introducing reactive oxidants (including catalytic intermediates) or by use of more aggressive reaction conditions. However, an obvious source of reactive oxidants remains underutilized. Specifically, many intermediates of the radical-chain autoxidation reactions that occur during the early (rapid) phase of wet oxidation processes (e.g., hydroxyl, HO·, and alkoxy, RO·, radicals) are highly energetic and highly reactive. Hence, if a wet oxidation reactor system is configured appropriately¹² (Figure 1), these reactive intermediates might be used to degrade recalcitrant products of partial oxidation. The criterion for synergistic rate acceleration is that the recirculated WAO-reaction products are consumed at a greater rate than can be accounted for by residence time alone.

Experimental evidence in support of this strategy was provided by Harrison and co-workers,¹³ who observed that the rate of *m*-xylene degradation was enhanced by the simultaneous addition of phenol, a more readily oxidized substrate. When phenol was present at appreciable concentrations, a "synergistic" rate enhance-

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ment was observed. Accordingly, once the phenol was depleted, the rate of *m*-xylene oxidation returned to its slow intrinsic value. Analogous "kinetic coupling" phenomena were noted by Boock and Klein¹⁴ in the high-temperature (300–380 °C) oxidation of mixtures of aliphatic alcohols and acetic acid. They reported that the rate of oxidation of acetic acid increased when simple alcohols such as ethanol were added. Similarly, Mahajani and co-workers^{3c} reported that the rate of degradation of acetic acid present as one of several compounds in an industrial waste stream was greater than that of acetic acid alone. The obvious explanation for these observations is that the recalcitrant compounds were oxidized by reactive intermediates generated during radical-chain autoxidation of the more readily oxidized substrates.

Moreover, the use of recirculation to enhance the effectiveness of wet oxidation was demonstrated in the context of an effluent-free (i.e., closed-mill) wood-pulp delignification technology currently under development in our laboratory.¹⁵ In the catalytic wet oxidation of lignin and polysaccharide fragments dissolved during wood-pulp processing, we observed a rapid decrease in the chemical oxygen demand (COD; mg of O₂/L) of the solution to one-third of its initial value in 0.5 h (150 °C, 0.7 MPa O₂, 0.5 M Na₅[PV₂Mo₁₀O₄₀]).^{15e} After the initial rapid-reaction phase, the rate of COD decrease slowed dramatically. As expected, low-molecular-weight organic compounds, including succinic and maleic acids (four-carbon dicarboxylic acids), were identified in the reaction mixture.¹⁶ However, upon further addition of untreated lignin and polysaccharide fragments, the recalcitrant products of partial oxidation were readily oxidized. The rate enhancement was tentatively attributed to oxidation of the recalcitrant compounds by reactive intermediates of Na₅[PV₂Mo₁₀O₄₀]-mediated radical-chain autoxidation reactions.^{15e,17-19}

We herein demonstrate that synergistic acceleration of the rate of COD decrease can be achieved by recirculation of WAO-reactor effluent. The observed oxidation greatly exceeds that expected on the basis of residence-time considerations alone. Moreover, correlations identified by use of a two-level, half-fraction factorial investigation are consistent with oxidation of recalcitrant WAO-reaction products by highly reactive intermediates generated during rapid radical-chain autoxidation of unreacted parent compounds. Finally, the experiments and data analysis described provide a convenient protocol for assessing specific synergistic rate enhancements that might be achieved by recirculation of particular WAO-reactor effluents.

The rate enhancement was quantified by extension of the lumped-parameter kinetic model applied to wet oxidation reactions by Li and Gloyna.²⁰ Individual organic compounds were oxidized by O₂ in the presence of Na₅[PV₂Mo₁₀O₄₀], a soluble polyoxometalate (POM) catalyst, and rates of wet oxidation were determined by measuring the COD of the solutions as a function of time. To demonstrate synergistic rate enhancement, the data were first analyzed using the general (lumped-parameter) kinetic model. In each case, a good fit between experimental and predicted COD values was obtained. After the initial rapid-reaction phase of each wet-oxidation reaction, additional unoxidized substrate was then added. In the absence of synergistic rate enhancement, subsequent changes in COD values with time continued to match those predicted by extension

of the lumped-parameter kinetic model. However, when synergistic rate enhancement occurred, experimentally determined COD values were substantially smaller than those predicted by the model. Design of the two-level, half-fraction factorial investigation is described in the Results and Discussion section.

Experimental Section

Materials and Apparatus. Equilibrium mixtures of sodium salts (pH values of 3.0–3.5) of the α -Keggin polyoxometalate anions α -Na_{3+*x*}[PV_{*x*}Mo_{12-*x*}O₄₀], where *x* = 1, 2, 3, with α -Na₅[PV₂Mo₁₀O₄₀] (*x* = 2, POM) the major species present, were prepared as previously reported.^{15e,21} D-Cellobiose, obtained from Aldrich, syringic acid, obtained from Alfa Aesar, potassium hydrogen phthalate (KHP; KC₈H₅O₄, 99.95%), obtained from Fisher Scientific, and phenol (99%), obtained from Mallinckrodt, were used without further purification. High-pressure gas cylinders containing oxygen (99+%) and nitrogen (99+%) were obtained from Badger Welding Supplies, Madison, WI. All experiments were performed in a 1-L pressure vessel (Parr Instrument Co., Moline, IL, model 4541) equipped with a gas-entrainment impeller. The gas-entrainment impeller was operated at 1200 rpm, at which no mass-transfer limitations were encountered.^{15e} For temperature control, a PID controller (model CN2010, Omega Engineering, Stamford, CT) was used. Unless otherwise stated, 0.93 MPa (135 psia) partial pressures of oxygen (at room temperature) were used.

Experimental Methods. In each experiment the reactor, containing water, POM, and oxygen, was heated to 155 °C and maintained at 155 ± 2 °C. At the desired temperature, concentrated 10 mL samples of organic compounds were injected under nitrogen pressure to provide specific COD values. Sampling was performed via a block-and-bleed system, with the sampling line purged at least twice before each sample was collected. For acquisition of kinetic data, samples were taken at regular intervals over several hours. Under the reaction conditions used, 1 h was sufficient for the rate of COD decrease to fall to a low value. To simulate the effect of recirculation of WAO-reactor effluent, "repeated-addition" experiments were performed: concentrated aliquots of the unoxidized organic compound were injected into the Parr reactor at 1-h increments (5–8 additions in total). Samples were removed for COD determination at the end of each 1-h reaction period, just prior to injection of the next aliquot. COD values were determined using Twist-Tube Accu-test vials obtained from Bioscience, Bethlehem, PA. Corrections for the total concentration of POM and for the concentration of reduced POM were made as previously described.^{15e} To avoid the addition of exogenous salts, natural ionic strengths and pH values were left unadjusted. Initial pH values of POM-containing solutions ranged from 3.0 to 4.5, with final pH values ranging from 2.7 to 4.4 (small decreases in pH were generally observed). For uncatalyzed reactions of cellobiose or phenol, initial pH values ranged from 5 to 7. In the absence of catalyst, little reaction, and hence little change in the pH values of the solutions, was observed. However, in the uncatalyzed reaction of syringic acid (4.2 mM), some reaction occurred and the pH of the solution decreased to 2.5 from an initial value of 3.2.

Mathematical Treatment of Reaction-Rate Data. The lumped-parameter model includes three catego-

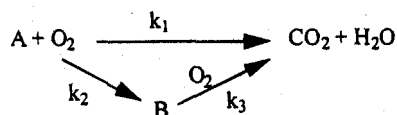


Figure 2. Reaction network for the lumped-parameter model of Li and Gloyna.^{20a}

ries: unreacted substrate (A), refractory products of partial oxidation (B), and the final products of complete oxidation, i.e., carbon dioxide and water (C) (Figure 2).

Along the upper pathway (Figure 2), the organic substrate is rapidly converted directly to carbon dioxide and water at a rate characterized by the rate constant k_1 . Alternatively, A is partially oxidized to refractory compounds, collectively labeled B (Figure 2). These compounds are slowly converted to carbon dioxide and water. Expressions describing the rates of decrease of A and B are given in eqs 1 and 2, where k_1 , k_2 , and k_3

$$-dC_A/dt = (k_1 + k_2)C_A^m[O_2]^n \quad (1)$$

$$-dC_B/dt = -\epsilon k_2 C_A^m[O_2]^n + k_3 C_B^p[O_2]^q \quad (2)$$

are rate constants, C_A is the concentration of A, C_B is the aggregate concentration of B, ϵ is the number of moles of B derived from 1 mol of A, and m , n , p , and q are orders of reaction. Lumped COD values are obtained, from C_A and C_B by introduction of the conversion factors α and β . These conversion factors are defined such that the products αC_A and βC_B are the COD values associated with 1.0 M solutions of A and B, respectively. Conversion of eqs 1 and 2 to COD units and summation give the change in COD as a function of time (eq 3), where it is assumed that the orders of reaction with respect to both O_2 and species A are identical for reactions 1 and 2 in Figure 2.

$$-dCOD/dt = \alpha(k_1 + k_2)C_A^m[O_2]^n - \epsilon\beta k_2 C_A^m[O_2]^n + \beta k_3 C_B^p[O_2]^q \quad (3)$$

In application of their general model, Li and Gloyna²⁰ treated the concentration of oxygen as a constant, and the orders of reaction with respect to A and B were both assigned a value of 1. With these assumptions and the use of an integrating factor, integration of eqs 1 and 2 (in units of COD) gives

$$COD = COD_A e^{-(k_1+k_2)t} + COD_B e^{-k_3 t} + COD_A \frac{\beta}{\alpha} \frac{\epsilon k_2}{k_3 - k_1 - k_2} \{e^{-(k_1+k_2)t} - e^{-k_3 t}\} \quad (4)$$

where COD_A and COD_B are the initial COD values attributed to A and B, respectively.²²

Data Analysis. For each model compound studied, orders of the reaction were determined by the method of initial rates. Initial rates were calculated as the difference between the initial COD of the solution and the first COD value measured, divided by the time elapsed between initiation of the reaction and removal of the first aliquot for analysis (typically 4–5 min). Orders of the reaction with respect to the concentrations (in COD values) of organic compounds were determined using a POM concentration of 0.05 M and an oxygen pressure of 0.93 MPa. The standard error (calculated by the LINEST function of Microsoft Excel) of the slope of the log–log plot of rate versus concentration was

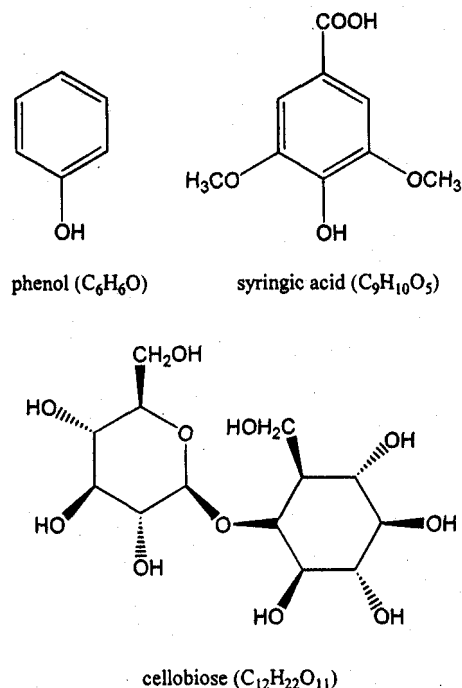


Figure 3. Model compounds which were investigated by WAO.

taken as the uncertainty in the reaction order. Because it could not be explicitly measured, the order of the reaction with respect to the COD associated with the refractory compounds, B, was assigned a value of unity. This assumption is consistent with application of the general model by Li and Gloyna.²⁰ Orders of the reaction with respect to the POM concentration and oxygen partial pressure were determined using concentrations of organic compounds associated with COD values of 1200 mg of O_2 /L. POM concentrations were then varied at constant initial O_2 pressures of 0.93 MPa, and P_{O_2} values were varied at constant POM concentrations of 0.05 M. The experimentally determined reaction orders were then employed in the calculation of the kinetic parameters in eqs 3 and 4. Two mathematical methods were used. In reactions of organic compounds for which the assumptions required to derive eq 4 were not applicable (i.e., $m \neq 1$), experimental COD values were fit to eq 3 using Microsoft Excel to perform the necessary numerical integrations. A simple Euler method (Dtime £ 1 min) was employed, and the results were independent of the magnitude of the time interval (for Dtime £ 1 min). The three parameters in eq 3 ($\alpha(k_1+k_2)$, $\epsilon\beta k_2$, and βk_3) were then determined by use of the Solver function in Microsoft Excel. In cases where eq 4 was applicable (i.e., $m = 1$, p is assigned a value of unity and P_{O_2} is constant), the kinetic parameters in eq 4 ($k_1 + k_2$, k_3 , and $\beta\epsilon k_2/\alpha$) were obtained by using the Solver function in Microsoft Excel to fit eq 4 to experimental COD values. For the model compounds studied, applicable equations (and mathematical methods) were used to analyze respective repeated-addition experiments. Details of the half-fraction, factorial study are provided in the Results and Discussion section.

Results and Discussion

Wet-oxidation experiments were carried out using three model compounds:²³ cellobiose, phenol, and syringic acid (Figure 3). Interest in these model compounds arose from our earlier studies^{15e} involving catalytic

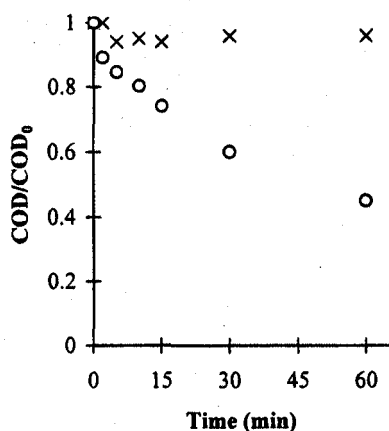


Figure 4. WAO of cellobiose. (O) $COD_0 = 1200$ mg of O_2/L (3.1 mM in cellobiose), $155^\circ C$, 0.05 M POM, initial oxygen pressure = 0.93 MPa. (x) $COD_0 = 2000$ mg of O_2/L , $155^\circ C$, no POM, initial oxygen pressure = 0.93 MPa.

oxidation of waste streams generated in the processing of wood pulp. In addition to serving as surrogates for the lignin and cellulose fragments present in those waste streams, these model compounds represent compounds present in many industrial waste streams.²³

The results are divided into three sections: (1) baseline kinetic analysis of POM-catalyzed wet-oxidation reactions of model compounds by fitting COD versus time data to Li and Gloyna's lumped-parameter model, (2) use of the kinetic parameters obtained in the baseline kinetic studies to quantify the rate enhancements obtained upon addition of parent (unreacted) model compounds to effluents obtained by WAO of the same parent compounds, and (3) a two-level, half-fraction factorial investigation of the experimental parameters responsible for the rate enhancement observed for cellobiose.

Wet Oxidation of Model Compounds. The WAO of cellobiose ($155^\circ C$ and 0.93 MPa O_2) was carried out in the absence of catalyst and in the presence of POM (0.05M). Decreases in COD values of the cellobiose solutions over 1 h are shown in Figure 4. While little reaction was observed in the absence of the catalyst, cellobiose reacted rapidly in the presence of POM. Even with POM present, however, the rate of reaction decreased significantly after the first hour (see Figure 6).

Orders of the reaction with respect to the concentrations of POM and cellobiose (in units of mg of O_2/L), and with respect to the partial pressure of O_2 , were determined by the method of initial rates (see Data Analysis in the Experimental Section). For cellobiose concentrations from 400 to 4000 mg of O_2/L (1.0–10 mM), the order of the reaction with respect to [cellobiose] was 1.4 ± 0.2 (Figure 5). POM concentrations and oxygen pressures were varied while keeping the initial concentration of cellobiose constant at 1200 mg of O_2/L (3.1 mM).

For POM concentrations from 0.0005 to 0.5 M and oxygen pressures from 0.38 to 2.85 MPa, orders of the reaction with respect to oxygen pressure and POM concentration were both near zero: 0.03 ± 0.11 for PO_2 and 0.01 ± 0.05 for [POM]. In all cases, the order of the reaction with respect to the decrease in COD associated with B (p in eq 3) was assigned a value of 1 (see the Experimental Section). The indicated values of the reaction orders were employed in a nonlinear least-squares regression analysis of the data to determine the kinetic parameters in eq 3. The resulting mathematical

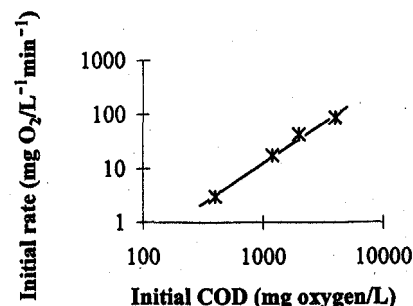


Figure 5. Apparent initial rate of WAO of cellobiose in the presence of 0.05 M POM, $155^\circ C$, initial oxygen pressure = 0.93 MPa. Order of reaction: slope of log-log plot = 1.4 ± 0.2 ; intercept = $\ln(k) = -7.7 \pm 0.7$ for k in units of mg of $O_2 \cdot L^{-0.4} \cdot min^{-1}$.

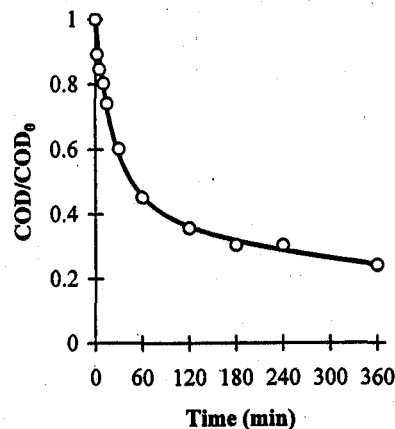


Figure 6. WAO of cellobiose. 0.05 M POM, $COD_0 = 1200$ mg of O_2/L (3.1 mM in cellobiose), $155^\circ C$, initial pressure of oxygen = 0.93 MPa. The solid line depicts the best-fit curve from eq 3, with $k_1 = 0.00126$ (mg of O_2/L)^{-0.4} min⁻¹, $k_2 = 0.00071$ (mg of O_2/L)^{-0.4} min⁻¹, and $k_3 = 0.00129$ min⁻¹, $m = 1.4$ (from Figure 5), $n = q = 0$ (determined experimentally), and p assumed to be unity.

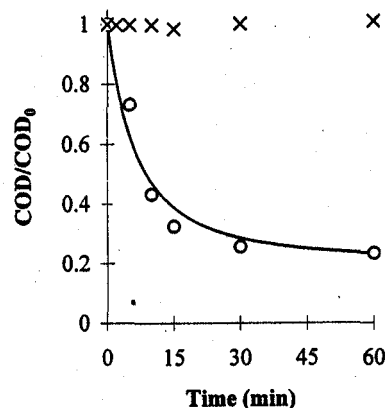


Figure 7. (O) WAO of phenol in the presence of 0.05 M POM. $COD_0 = 1200$ mg of O_2/L (5.4 mM in phenol), $155^\circ C$, initial oxygen pressure = 0.93 MPa. (x) WAO of phenol in the absence of a catalyst at the same temperature, initial oxygen pressure, and phenol concentration. The solid line depicts the best-fit curve for the POM-catalyzed reaction; $k_1 = 0.00284$ (mg of O_2/L)^{-0.5} min⁻¹, $k_2 = 0.00088$ (mg of O_2/L)^{-0.5} min⁻¹, and $k_3 = 0$; $m = 1.5$, and $n = 0$ (determined experimentally).

model (solid line in Figure 6) provides an excellent fit of the experimental data (open circles) for 3.1 mM cellobiose (see the figure caption for additional details).

Experimental COD values for the WAO of phenol ($155^\circ C$ and 0.93 MPa O_2) are shown in Figure 7. In the absence of POM, no reaction was observed. The low reactivity of phenol under the conditions used is consistent with previous observations.^{13,23c} In the presence

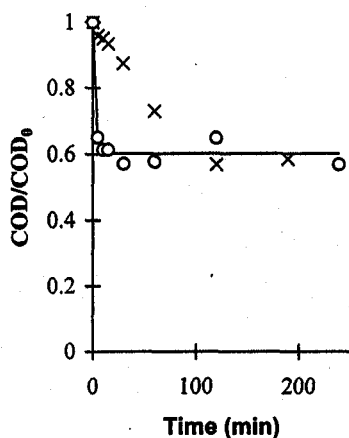


Figure 8. (O) WAO of syringic acid in the presence of 0.05 M POM. $COD_0 = 1200$ mg of O_2/L (4.2 mM in syringic acid), 155 °C, initial oxygen pressure = 0.93 MPa. (x) WAO of syringic acid in the absence of a catalyst at the same temperature, initial oxygen pressure, and syringic acid concentration. The solid line depicts the best-fit curve for the POM-catalyzed reaction; $k_1 = 0.217$ min $^{-1}$, $k_2 = 0.238$ min $^{-1}$, and $k_3 = 0$; $m = 1$, and $n = 0$ (determined experimentally).

of POM, however, the COD values decreased rapidly during the first half hour of the reaction period. At longer reaction times, however, the reaction rate decreased to a low value as the phenol was progressively converted to less reactive products of partial oxidation. The initial rate measurements indicated that the order of the reaction with respect to [phenol] was 1.5 ± 0.3 (400–4000 mg of O_2/L ; 1.8–17.9 mM phenol).

POM concentrations and oxygen pressures were varied while keeping the initial concentration of phenol constant at 1200 mg of O_2/L (5.4 mM). For POM concentrations from 0.05 to 0.5 M and oxygen pressures from 0.38 to 0.93 MPa, the orders of the reaction with respect to PO_2 and [POM] were both near zero. The best-fit curve for the POM-catalyzed wet oxidation of phenol was calculated using the mathematical form of eq 3. Good agreement was obtained between calculated values (Figure 7, solid line) and experimental values (open circles; 1200 mg of O_2/L of phenol).

Even in the absence of POM, syringic acid initially reacted at a significant rate with oxygen (Figure 8). In the presence of POM, there was a very rapid initial decrease in COD values, followed by early onset of a slow-reaction phase. After the onset of the slow phase, the rate of decrease in COD values was notably small. Unlike the case for cellobiose or phenol, the POM-catalyzed wet-oxidation reaction was first order (1.1 ± 0.2) in [syringic acid] (400–4000 mg of O_2/L ; 1.4–14 mM). For POM concentrations from 0.05 to 0.5 M and oxygen pressures from 0.38 to 0.93 MPa, the orders of the reaction with respect to PO_2 and [POM] were both near zero (1200 mg of O_2/L ; 4.2 mM syringic acid). These reaction orders were used to determine the kinetic parameters in eq 4. For the POM-catalyzed wet oxidation of syringic acid (1200 mg of O_2/L), good agreement was obtained between the COD values calculated using eq 4 (Figure 8, solid line) and the experimental values (open circles).

Repeated Addition of Model Compounds. To model the effects of effluent recirculation, repeated-addition WAO experiments were performed. In the repeated-addition experiments, 10-mL aliquots of a concentrated aqueous solution or slurry of the model compound were injected (using nitrogen-gas pressure)

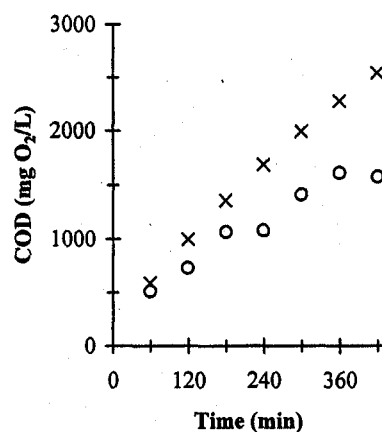


Figure 9. Comparison of COD values predicted using eq 3 (no synergistic rate enhancement) (x) and actual COD values (O) for the repeated-addition WAO of cellobiose. 155 °C, initial oxygen pressure = 0.93 MPa, 1200 mg of O_2/L (3.1 mM cellobiose) added at the start of each cycle, [POM] = 0.05 M. Because of the synergistic rate enhancement, the actual COD values (O) lie below those accounted for by residence time alone (x).

into the wet-oxidation reactor at 1-h intervals. At a reaction temperature of 155 °C, all three model compounds used—cellobiose, phenol, and syringic acid—were fully dissolved. After injection of the first aliquot of organic compound, the volume of liquid inside the reactor was 0.5 L. Upon addition of each aliquot, the COD of the solution inside the reactor increased in a stepwise fashion and then decreased over the subsequent 1-h interval. The time interval of 1 h was chosen to provide sufficient time for completion of the early rapid-reaction phase and for refractory products of partial wet oxidation to accumulate. Samples were removed for analysis (COD) at the end of each 1-h time period prior to injection of the next aliquot. Relative to total volumes and concentrations, the cumulative experimental error associated with sampling, injection of aliquots, and incidental evaporation was negligible (less than 2.5% per aliquot).

In the first repeated-addition experiment, 10-mL aliquots of 0.156 M cellobiose (which provided 1200 mg of O_2/L increases in total COD values) were injected into the reactor at 1-h intervals. The experimental conditions (155 °C, 0.93 MPa O_2 , and 0.05 M POM) were the same as those used in the kinetic experiments described above. The total COD values of the solution measured after each 1-h reaction period are plotted in Figure 9 (open circles).

Predicted COD values were calculated using the reaction orders and kinetic parameters obtained from study of the WAO of cellobiose (i.e., Figures 4–6). Equation 3 was then used to calculate the total COD expected at the end of each 1-h interval after addition of substrate. Each individually calculated COD value is indicated by an x in Figure 9. Notably, actual COD values were significantly smaller than those predicted using eq 3. After each 1-h reaction period, only recalcitrant WAO products remain. Had no synergistic enhancement occurred upon subsequent addition of cellobiose, COD values would have simply decreased with residence time as predicted using eq 3 (cf. Figure 11). Thus, the smaller than predicted COD values shown in Figure 9 demonstrate enhanced reaction of the recalcitrant WAO products.

Similar results were obtained using phenol (1200 mg of O_2/L , 5.4 mM, per aliquot added; Figure 10). As with

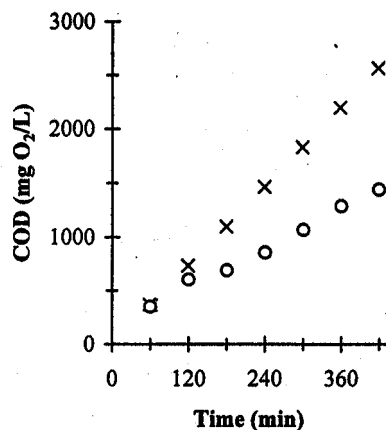


Figure 10. Comparison of COD values predicted using eq 3 (no synergistic rate enhancement) (x) and actual COD values (O) for the repeated-addition WAO of phenol. 155 °C, initial oxygen pressure = 0.93 MPa, 1200 mg of O₂/L (5.4 mM of phenol) added in each cycle, [POM] = 0.05 M.

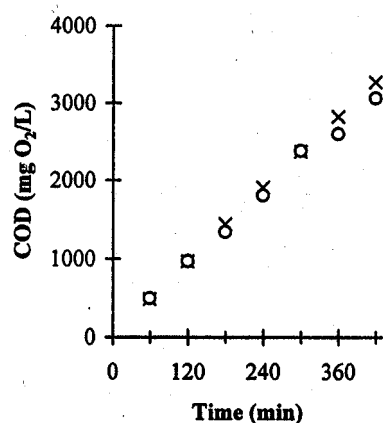


Figure 11. Comparison of COD values predicted using eq 4 (no synergistic rate enhancement) (x) and actual COD values (O) for the repeated-addition WAO of syringic acid. 165 °C, initial oxygen pressure = 0.93 MPa, 1200 mg of O₂/L (4.2 mM) added in each cycle, [POMI] = 0.05 M. In the absence of synergistic rate acceleration, experimental COD values (O) match those predicted on the basis of additional residence time alone (x).

cellobiose (Figure 9), actual COD values (open circles in Figure 10) were significantly smaller than those predicted using eq 3. This negative deviation again indicates that, in the presence of added phenol, the recalcitrant WAO products were consumed at an enhanced rate.

A very different result was obtained using syringic acid (4.2 mM, 1200 mg of O₂/L per aliquot; Figure 11). In contrast to the results observed using cellobiose or phenol, COD values measured at the end of each 1-h interval increased in a linear fashion. Moreover, actual COD values (open circles) agreed closely with those predicted using eq 4. (Equation 3, which is more general than eq 4, gives an analogous result.) The close agreement shows that no enhanced consumption of recalcitrant WAO products occurred. When these results are compared with those obtained using cellobiose or phenol, it is noteworthy that the order of the reaction with respect to [syringic acid] was close to unity. By contrast, higher order noninteger values near 1.5 were found for the reaction order with respect to [cellobiose] and [phenol]. Although the paucity of the data does not permit one to draw firm conclusions, the difference in reaction orders might reflect a fundamental difference between the mechanism for POM-catalyzed oxidation

of syringic acid and those for cellobiose and phenol. The observed reaction orders with respect to cellobiose and phenol may indicate a reaction mechanism involving initiation and propagation of free-radical species. (Half-integer orders are frequently observed for reactions which proceed by free-radical mechanisms.) The reactions of the free-radical species with refractory compounds are a likely mechanism for the enhanced oxidation observed here (see Figures 9 and 10). Conversely, the order of the reaction with respect to syringic acid was near unity. In this case no enhancement of the rate of oxidation was observed (Figure 11). One explanation for the documented difference between cellobiose and phenol versus syringic acid and consistent with these reaction orders is that, under the experimental conditions chosen, oxidation of cellobiose and phenol occurs via radical-chain autoxidation reactions that involve a relatively high number of chain-propagation steps before termination, while syringic acid is oxidized via a less extensive sequence of elementary reaction steps to give intermediates that are relatively stable. Apparently, repeated addition of syringic acid under these mild conditions results in oxidation of the newly added material to relatively stable intermediates without providing a concentration of reactive chain-propagation intermediates sufficiently high for observation of enhanced oxidation of the intermediates already present in solution. It is also possible that rate enhancement might be observed for syringic acid under a different set of reaction conditions. Nonetheless, the close agreement between the observed COD values and those predicted by eq 4 (see Figure 11) confirms the validity of the kinetic model. Moreover, comparison of Figures 9–11 demonstrates the usefulness of the experimental protocol for rapid evaluation of the rate enhancements that might result from the recirculation of specific WAO-reactor effluents.

Half-Fraction Factorial Investigation of the Synergistic Rate Enhancement of Cellobiose Oxidation. Experimental Design.

In the repeated addition of cellobiose (Figure 9), actual COD values were substantially smaller than those predicted by eq 3. A two-level, half-fraction experimental design (2⁴⁻¹) was used^{24a} to identify the experimental parameters that correlated most strongly with the observed rate enhancement. For this experimental design, only two sequential additions of cellobiose—rather than multiple additions—were required. First, an aliquot of cellobiose (which provided a COD value designated COD') was injected at *t* = 0 min and reacted at 155 °C for 89 min (reaction period 1). The first reaction period was of sufficient duration for refractory species to form and for the rate of wet oxidation to decrease to a low value. The COD at the end of reaction period 1 was designated COD₈₉. The second reaction period was used to assess the extent to which the refractory compounds (COD₈₉) reacted after an additional aliquot of cellobiose (COD'') was introduced. The second aliquot of cellobiose was introduced at *t* = 90 min (1 min after the end of reaction period 1). The COD of the solution 90 min after the start of the second reaction period was designated COD₁₈₀. A typical reaction profile is shown in Figure 12.

The roles of four experimental parameters, referred to as the "main effects", were investigated (Table 1): the COD associated with cellobiose introduced at the start of reaction period 1 (COD'), the COD associated with cellobiose added at the beginning of reaction period 2

Table 1. Experimental Conditions and Extent of Enhanced Oxidation (d, from Eq 5) for a Two-Level, Half-Fraction Factorial Study of Recirculated Effluent from the WAO of Cellobiose at 155°

run no.	concn of cellobiose in reaction period 1 (mg of O ₂ /L)	concn of cellobiose in reaction period 2 (mg of O ₂ /L)	concn of POM(M)	pressure of oxygen (MPa)	d
1	—	—	—	—	0.46
2	+	—	—	+	0.79
3	—	+	—	+	0.08
4	+	+	—	—	0.60
5	—	—	+	+	0.18
6	+	—	+	—	1.08
7	—	+	+	—	0.00
8	+	+	+	+	0.31
upper level (+)	5000	5000	0.05	2.85	
lower level (—)	1000	1000	0.0005	0.38	

Table 2. Effects of Four Experimental Parameters (Main Effects) on Synergistic Rate Enhancement (d, from Eq 5) during the Recirculation of Effluent from the WAO of Cellobiose

parameter	estimate of effect	significant?
mean value	0.438	
concn of cellobiose in reaction period 1	0.511	yes
concn of cellobiose in reaction period 2	-0.381	yes
concentration of POM	-0.089	no
oxygen pressure	-0.197	no
95% CI for the four main effects (3 degrees of freedom)	0.229	

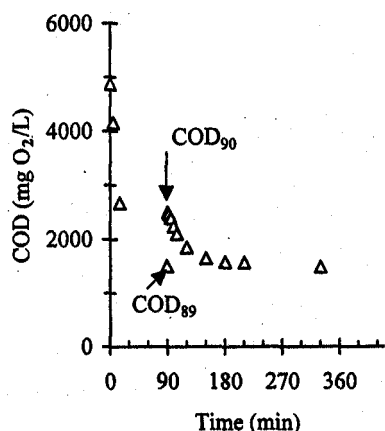


Figure 12. Reaction profile for WAO of cellobiose in two reaction periods, representing recirculation of WAO effluent. COD at the start of the first reaction period was 5000 mg of O₂/L (13 mM cellobiose); additional cellobiose (1000 mg of O₂/L, 2.6 mM) was added at the start of the second reaction period; [POM] = 0.0005 M; oxygen pressure = 2.85 MPa.

(COD), the concentration of POM ([POM]), and the partial pressure of oxygen (P_{O₂}).

An assumption implicit in this use and analysis of the 2⁴⁻¹ half-fraction design is that three-factor interactions are negligible.^{24a} In addition, with this half-fraction design, two-factor interactions are confounded with one another. Consequently, individual two-factor interactions such as AB or CD, where A, B, C, and D are the four parameters (main effects) investigated, cannot be estimated. However, the sums of confounded two-factor interactions (e.g., the sum AB + CD) can be calculated. The threshold value for the statistical significance of each main effect, at a 95% confidence level, was calculated from the sums of confounded two-factor interactions. To minimize time-dependent biases, the eight experiments required by this design were performed in random order. During each of the eight experiments, four samples were removed for COD analysis during reaction period 1, and at least 10 samples were removed during reaction period 2.

To draw quantitative conclusions from the half-fraction study, it was necessary to define an additional

parameter, δ , which was used to indicate the extent to which enhanced oxidation occurred during the second reaction period. This parameter was defined using a ratio: the actual COD increase during reaction period 2 (COD₁₈₀ - COD₈₉) divided by the amount the COD would have increased had no enhanced oxidation occurred (eq 5). An analogous approach was used by Harrison and co-workers¹³ to define the synergistic rate enhancement observed in the WAO of mixtures of phenol and *m*-xylene.

$$\delta = 1 - \frac{\text{COD}_{180} - \text{COD}_{89}}{-(90 \text{ min})(k_{\text{slow}})(\text{COD}_{89}) + \gamma \text{COD}''} \quad (5)$$

The difference in the numerator of eq 5 is the experimentally observed change in COD during reaction period 2. The two terms in the denominator sum to the amount the COD would have changed during reaction period 2 had no enhanced oxidation occurred. At the end of reaction period 1, the solution contained refractory species (COD₈₉). At the beginning of reaction period 2 ($t = 90$ min), cellobiose (COD'') was added. Hence, the total COD at the start of reaction period 2 was COD₈₉ + COD''. Had no enhanced oxidation occurred, the net change in COD during the second reaction period would have equaled the sum of the changes in COD values associated with two independent (i.e., nonkinetically coupled) reactions. These changes in COD values are each represented by a term in the denominator of eq 5: (1) a decrease in COD associated with the continued wet oxidation, from $t = 90$ to 180 min, of COD' (i.e., an additional 90 min of wet oxidation of COD₈₉ alone at a rate dictated by k_{slow}) and (2) an increase in COD associated with the introduction and 90 min wet oxidation (the duration of reaction period 2) of COD alone.

The rate constant k_{slow} was calculated by dividing the COD decreases observed from $t = 180$ to 330 min (under the reaction conditions corresponding to each of the eight runs; Table 1) by the elapsed time (150 min). In all cases, changes in COD values during this time period, and hence k_{slow} values, were small (cf. the change in COD from $t = 180$ to 330 min in Figure 12). As a result, uncertainties in δ (eq 5) attributable to use of a

first-order approximation for k_{slow} were negligible. Values used for the second term in the denominator of eq 5 were determined directly by wet oxidation of cellobiose at concentrations equal to the upper and lower COD'' values for 90 min under the reaction conditions used in the eight runs. The experimentally determined scaling factor, g , was defined so that $gCOD''$ corresponded to the fraction of COD'' left after each 90-min control reaction. Finally, eq 5 is written in a form that assigns a value of zero to d when no rate enhancement is observed. Values of d greater than 0 indicate rate enhancement; negative values would indicate inhibition.

Impacts of Experimental Variables. A value for d was calculated for each of the eight runs described in Table 1. The mean value of 6 and the impacts (positive and negative) of the four experimental variables on 6 were calculated using the Yates algorithm^{24b} (Table 2). Comparison of the magnitudes of the calculated impacts with that of the 95% confidence interval (CI) was used to determine if the experimental variables were significant. A five-fold increase in the concentration of cellobiose introduced at the beginning of the first reaction period (COD') resulted in a statistically significant increase in 6 (a positive impact of 0.510 compared to the CI of 0.229; Table 2). A five-fold increase in the concentration of cellobiose injected at the beginning of the second reaction period (COD'') had a negative impact (-0.380) on 6. Within the range of POM concentrations used (0.0005–0.05 M), no correlation between POM concentration and 6 was found. This lack of correlation between POM concentration and 6 is consistent with the zero-order dependence of the initial reaction rate on catalyst concentration (see Figures 4–6 and eq 3). The effect of O₂ partial pressure on d was less clear. The negative impact of -0.197 was somewhat smaller than the CI (0.229).

The increase in 6 (large positive impact of 0.510) associated with the five-fold increase in COD is consistent with the rate enhancements observed in the uncatalyzed oxidations of model-compound mixtures by Harrison and co-workers¹³ and Klein.¹⁴ Klein reported that the initial rate of oxidation of acetic acid was enhanced by the addition of ethanol, while acetic acid suppressed the rate of oxidation of ethanol. These results suggest that acetic acid was able to compete effectively for the highly reactive intermediates generated during the wet oxidation of ethanol. Similarly, in the present investigation the positive impact of COD values on 6 suggests that the recalcitrant species formed during reaction period 1 compete for the highly reactive intermediates generated following subsequent addition of cellobiose (COD) at the beginning of reaction period 2.

An increase in COD was associated with a negative impact on 6. In studies of multicomponent mixtures, Klein¹⁴ also noted that rates of wet oxidation failed to follow simple monotonic dependencies on total concentrations of organic compounds. (In particular, at certain concentrations, suppression rather than enhancement was observed.) Given the complexity of wet-oxidation reactions, any hypothesis regarding the basis for the negative impact of the five-fold increase in COD (from 1000 to 5000 mg of O₂/L), observed in the present study, must be regarded as tentative. Nonetheless, the negative impact is consistent with competition between refractory species (COD₈₉) and unreacted cellobiose (COD'') for reaction with highly reactive intermediates.

At the lower level of added cellobiose (COD'' = 1000 mg of O₂/L), the recalcitrant species that constitute the COD₈₉ value can compete effectively for highly reactive intermediates. At the upper COD level (5000 mg of O₂/L), however, the ratio of COD₈₉ to COD'' is sufficiently small that the recalcitrant species present compete less effectively with cellobiose.

Conclusions

Under moderate conditions (155 °C, P_{O_2} less than 1.0 MPa, and POM-catalyst concentrations as small as 0.0005 M), additions of cellobiose or phenol to solutions containing recalcitrant products of incomplete WAO resulted in enhanced oxidation of the recalcitrant compounds (low-molecular-weight acids). The results of a half-fraction factorial investigation were consistent with oxidation of the recalcitrant compounds by highly reactive intermediates generated during radical-chain autoxidation of the added compounds. Together, these results show that enhanced oxidation of recalcitrant WAO-reaction products might be achieved by partial recirculation of industrial wet-oxidation reactor effluents. This approach might also be used to advantage in the reclamation of process water in closed operations wherein full recirculation of WAO-reactor effluents is required.

Acknowledgment

The authors thank the U.S. Department of Energy Office of Industrial Technologies (DE-FC36-95GO10090) and member companies of the USDA Forest Service, Forest Products Laboratory, Polyoxometalate Bleaching Consortium, for support and Cyprus Climax Molybdenum Corp. and Shieldalloy Metallurgical Corp. for gifts of molybdenum and vanadium.

Nomenclature

- A = organic species which are readily oxidized in wet air oxidation
- B = organic species which are difficult to oxidize in wet air oxidation
- C_i = concentration of species i
- CI = confidence interval
- COD _{t} = chemical oxygen demand (mg O₂/L) at time t
- COD = COD added in the first reaction period for two-stage experiments
- COD = COD added in the second reaction period for two-stage experiments
- k_i = reaction rate constant ($i = 1, 2$, or 3) in the model of Li and Gloyna^{20a}
- k'_i = pseudo-first-order reaction rate constant which incorporates the dependence of the reaction rate on: the concentration of the oxidant, e.g., $k'_1 = k_1[O_2]^n$
- k_{slow} = reactivity of recalcitrant species from partial oxidation of cellobiose
- m, n, p, q = reaction orders with respect to concentrations of organic species and O₂
- POM = soluble polyoxometalate catalyst
- P_{O_2} = oxygen pressure
- t = time, min
- WAO = wet air oxidation
- a = chemical oxygen demand of 1 mol of species A
- β = chemical oxygen demand of 1 mol of species B
- g = fraction of chemical oxygen demand remaining after 90 min of reaction
- d = extent of enhancement of mineralization of recalcitrant species

e = number of moles of B derived from the wet oxidation of 1 mol of A

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(22) Equation 4 differs slightly from the integrated rate expression used by Li and Gloyna (ref 20a) in that it includes the terms α , β , and ϵ . The terms α and β were included to allow more explicitly the COD value associated with 1 mol of A to differ from that associated with 1 mol of B. Inclusion of the term ϵ (related to the "point selectivity" described by Li and Gloyna) more explicitly assigns an aggregate stoichiometry to the conversion of A to B. In application, however, eq 4 is functionally equivalent to the expression used by Li and Gloyna.

(23) Additional examples of investigations of model compounds include refs 2a,c,h, 3a, 6a,b, 8a–c, 13, 14, and 20a and the following: (a) Collivignarelli, C.; Bissolotti, G. Experiences in the Treatment of Hazardous Wastes by Wet Oxidation. In *Proceedings of the 5th International Solid Wastes Conference*; Anderson, L., Moeller, J., Eds.; Academic Press: London, 1988; pp 219–227. (b) Skaates, J. M.; Briggs, B. A.; Lamparter, R. A.; Baillod, C. R. Wet Oxidation of Glucose. *Can. J. Chem. Eng.* **1981**, *59*, 517–521. (c) Joglekar, H. S.; Samant, S. D.; Joshi, J. B. Kinetics of Wet Air Oxidation of Phenol and Substituted Phenols. *Water Res.* **1991**, *25*, 135–145. (d) Pruden, B. B.; Le, H. Wet Air Oxidation of Soluble Components in Waste Water. *Can. J. Chem. Eng.* **1976**, *54*, 319–324. (e) Gassó S.; Baldasano, J. M.; González, M.; Abatzoglou, N.; Lemonnier, J. P.; Chornet, E. Wet Oxidation via Two-Phase Flow Reactors and High Mass-Transfer Regimes. *Ind. Eng. Chem. Res.* **1992**, *31*, 2057–2062. (f) Tukac, V.; Hanika, J. Catalytic Wet Oxidation of Substituted Phenols in a Trickle Bed Reactor. *J. Chem. Technol. Biotechnol.* **1998**, *71*, 262–266. (g) Kabyemela, B. M.; Takigawa, M.; Adschiri, T.; Malaluan, R. M.; Arai, K. Mechanism and Kinetics of Cellobiose Decomposition in Sub- and Supercritical Water. *Ind. Eng. Chem. Res.* **1998**, *37*, 357–361.

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Received for review February 26, 1999
Revised manuscript received October 4, 1999
Accepted October 8, 1999

IE990149N