Degradation of Pulp-Mill Effluent by Oxygen and Na$_5$[PV$_2$Mo$_{10}$O$_{40}$], a Multipurpose Delignification and Wet Air Oxidation Catalyst

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Water-soluble salts of polyoxometalate (POM) anions can be used as (net) catalysts for selective, effluent-free oxygen delignification (bleaching) of unbleached kraft wood-pulps. Essential to this process is the use of the POM anions as catalysts for the wet oxidation of the lignin removed from the pulp fibers. In anaerobic bleaching, a 0.5 M solution of α-Na$_5$[PV$_2$Mo$_{10}$O$_{40}$] (POM$_{ox}$) is combined with wood pulp and the mixture heated to 125 °C. This treatment dissolves certain organic compounds (some lignin and polysaccharide fragments) with a combined chemical oxygen demand (COD) of 1500–2000 mg of O$_2$/L. Before the solution can be used again for bleaching, the POM anions (POM$_{red}$) must be deoxidized and the dissolved organic compounds removed. Here, a second function of the POM anions is realized. They are used under mild conditions (150 °C, 0.7 MPa of O$_2$) to catalyze the wet air oxidation of the dissolved organic compounds. After several cycles of anaerobic bleaching and wet oxidation, a steady-state condition in COD (at ca. 550 mg of O$_2$/L) is achieved.

Introduction

Wood consists primarily of polysaccharides (cellulose and hemicelluloses) and lignin. Lignin, which constitutes roughly 20–35% by weight of most woods, is a complex, highly cross-linked hydroxylated and methoxylated phenylpropane polymer (Fengel and Wegener, 1984). In the manufacture of paper, individual wood cells, or fibers, are fit separated from one another in a pulping process, bleached, and finally formed into thin sheets.

Pulps can be made in two ways, either by mechanical separation of wood fibers (mechanical pulps) or by the chemical removal of lignin (chemical pulps) (Sjostrom, 1992). A high proportion of the chemical pulps produced in the United States end in much of Europe is manufactured using the kraft process. Here, 80-90% of the lignin is removed by cooking the chipped wood at a high temperature (170 °C) in an aqueous solution of sodium hydroxide and sodium sulfide. Kraft pulping is an effluent-free process; lignin removed during the cook is converted to carbon dioxide and water in a process that converts organic and inorganic sulfur compounds back to sodium sulfide.

The purpose of bleaching is to remove the residual lignin from the fibers that remains after pulping. It is here that a major technological challenge arises. Although chlorine and its compounds are the most effective chemicals currently available for bleaching chemical wood pulps, the use of these oxidants results in the generation of a variety of chlorinated organic compounds (Singh, 1979; Gierer, 1982). Those that survive wastewater treatment at the mill are eventually released into the environment. The challenge is, thus, to eliminate the need for bleaching chemicals that produce persistent and potentially toxic byproducts. In addition, many in the pulp and paper industry expect that the release of any organic waste (other then carbon dioxide) into the environment will eventually be banned altogether. Hence, there is an additional need for the development of an effluent-free "closed" bleaching process from which few, if any, chemical waste products, other than carbon dioxide and water, are released (Hintz, 1993).

As a bleaching agent, oxygen is the most attractive alternative is chlorine and chlorine dioxide with respect to both the environment and cost. However, difficulties arise in the use of oxygen, either as a delignifying agent or in the wet oxidation of pulp-mill waste streams. First, when oxygen is used as a delignifying agent and applied directly to pulp slurries in water, a number of reduced oxygen species are formed. These species include superoxide radical anions (OO^{2-}), peroxide anions (HOO$^-$), hydroxyl radicals (HO$^{\cdot}$), and the analogous alkyl derivatives, ROO$^{\cdot}$, ROO$^-$, and RO$^{\ddot{z}}$. Some of these, such as HO$^{\cdot}$ and RO$^{\ddot{z}}$, show very little selectivity for lignin as they react rapidly with cellulose as well (Gellerstedt et al., 1986). Such reactions can lead to unacceptable degradation of pulp fibers. Second, it has long been recognized that wet air oxidation can be used to reduce the chemical oxygen demand of organic waste streams (Teletzke et al., 1964). A difficulty normally encountered in these processes, however, is that organic materials are converted to low molecular weight acids, whose conversion to carbon dioxide and water requires high temperatures and long reaction times (Li et al., 1991). Wet oxidation processes were recently reviewed by Joshi and co-workers (Mishra et al., 1995).

Both problems might be overcome by the use of transition-metal-baaed catalysts. In general, however, the behavior and reactivity of transition-metal ions in water, the solvent of choice for pulp processing, are difiicult to control (Baes and Mesmer, 1976). In addition, many transition-metal oxides and hydroxides have limited solubilities in water such that the metal ions are rapidly lost from solution as solid precipitates. One class of transition-metal catalysts, however, polyoxometalates (POMs, polymeric metal oxide anions), are both well-behaved in water and remarkably stable toward oxidative degradation.

Applications of POM complexes in oxidation catalysis have recently been reviewed (Pope and Miiller, 1991; Hill and Presser-McCartha, 1995; Okuhara et al., 1996). Several members of this class of materials have proven highly selective in the delignification of kraft pulp (Weinstock et al., 1996; Weinstock and Hill, 1996). Herein is the first detailed report of the use of a POM bleaching agent, Na$_5$[PV$_2$Mo$_{10}$O$_{40}$], as a catalyst for the wet oxidation of lignin-containing bleach liquors. Brief accounts of this process concept, along with some preliminary data, have previously been reported (Atalla
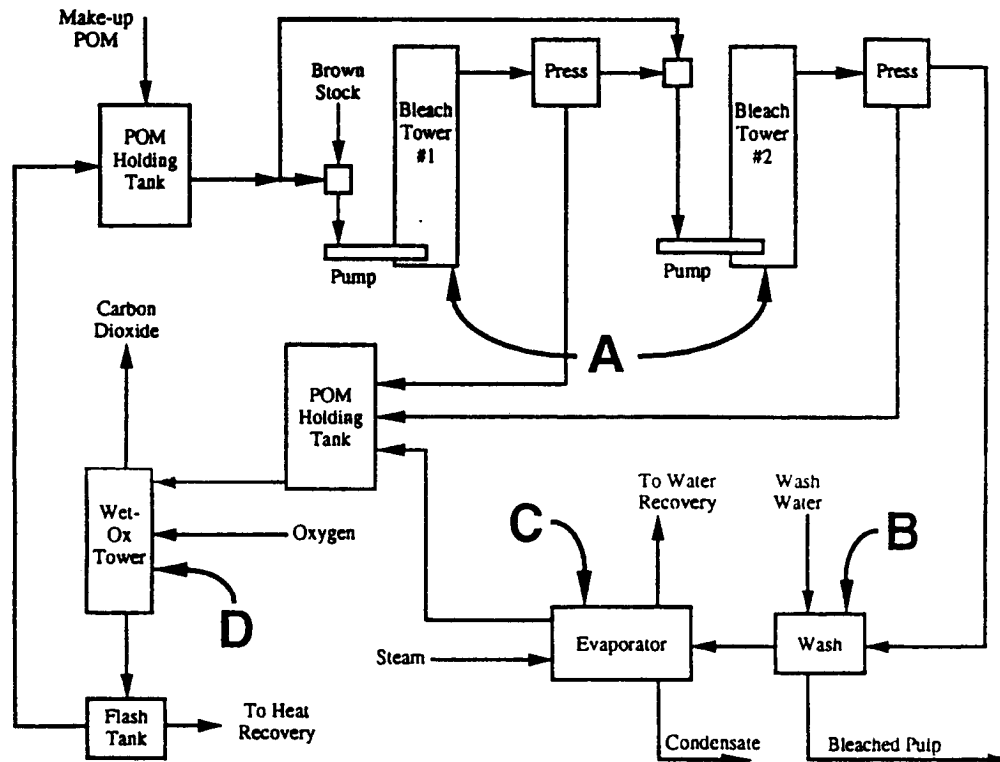
Figure 1. Schematic diagram of an effluent-free POM bleaching mill consisting of four unit operations: A, bleaching; B, pulp washing; C, evaporation of wash water and removal of non-process elements; D, wet oxidation and POM reoxidation.
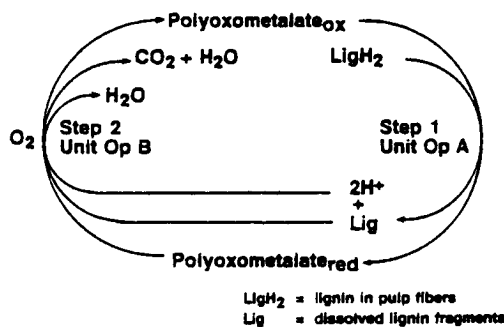
Figure 2. Two chemical steps (unit operations A and D) that sum to the net conversion of residual lignin in wood-pulp fibers to carbon dioxide and water.

et al., 1996; Weinstock et al., 1996, 1997; Weinstock and Hill, 1996).

Use of Polyoxometalates and Oxygen for Effluent-Free Delignification. As currently envisioned an effluent-free POM bleaching mill will include four key unit operations: (A) bleaching; (B) pulp washing; (C) removal of wash water and undesired inorganic salts; and (D) POM-catalyzed wet oxidation of dissolved organic materials and simultaneous regeneration of the POM to its bleaching-active form (Figure 1).

In bleaching (unit operation A, Figure 1), pulp is slurried in an aqueous POM solution and the mixture heated. Residual lignin in the pulp fibers is oxidized directly by the POM, which is thereby reduced (step 1, Figure 2). To avoid exposure of the pulp fibers to oxygen-centered radicals, this step is carried out under anaerobic conditions.

The used liquor, now containing reduced POM and dissolved lignin fragments, is transferred through unit operations B end C (discussed in Atalla et al., 1996) to the wet oxidation reactor (unit operation D, Figure 1). The purpose of unit operation D is two-fold to oxidatively degrade dissolved lignin to carbon dioxide and

water and to reoxidize the POM to its active form (step 2, Figure 2). The sum of unit operations A and D (steps 1 and 2) is the selective conversion of residual lignin in the pulp fibers to carbon dioxide and water:

$$\text{residual lignin} + O_2 \xrightarrow{\text{POM}} CO_2 + H_2O \qquad (1)$$
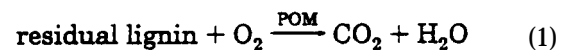
Upon cessation of the wet oxidation reactions, the liquor, now containing the POM in its oxidized (bleaching-active) state, is ready for return to unit operation A.

In the wet oxidation of pulp-mill end many other organic waste streams, high temperatures and oxygen pressures are required to reduce chemical oxygen demand (COD) levels to near zero (Shende et al., 1994). In some cases, rapid initial decreases in COD are at preceded by a slow induction phase (Willms et al., 1987). Once the wet oxidation reactions begin in earnest, rapid decreases in the COD are often observed. However, as the organic compounds present initially are converted to more refractory ones, the rate at which the COD decreases declines significantly (Lin et al., 1996). Transition-metal catalysts can increase the rate of consumption of the more refractory species resulting from partial oxidation reactions (Levec and Pintar, 1995). A number of catalyst systems (both soluble and heterogeneous) are effective for this purpose (Miahra et al., 1995). Another means of enhancing the consumption of the less readily oxidized compounds, i.e., the more refractory species, is to add an easily oxidized compound, e.g., phenol, to the reaction mixture. This phenomenon is referred to by some authors as a "synergistic" effect (Williams et al., 1987). The easily oxidized compound is a readily available source of the electrons necessary for initiation of radical-chain autoxidation processes. It is probable that some of the intermediates involved in these processes are sufficiently reactive to oxidize the more refractory substrates. A similar strategy is used in homogeneous catalytic oxidation by dioxygen (O_2),

wherein a "sacrificial reductant" is added to supply electrons for the transition-metal-mediated reduction of dioxygen to more reactive metal-oxygen intermediates (Hamilton, 1974). In the wet oxidation of POM bleaching liquors, the POM anion, reduced during anaerobic lignin oxidation, can react directly with oxygen to rapidly initiate radical-chain autoxidation reactions (Duncan and Hill, 1997; Kozhevnikov et al., 1981). The POM can also serve as a catalyst for accelerating the overall reaction rate (Kozhevnikov et al., 1981; Bassam et al., 1989; Neumann and Levin, 1992). Furthermore, a synergistic enhancement of wet oxidation might result from the addition of lignin fragments, freshly dissolved in unit operation A, to unit operation D.

Because the POM solution is in constant circulation, the concentration of dissolved lignin would rise to unacceptable levels if a means for removing this material were not in place. However, it is not necessary that the COD of the POM bleaching liquor be reduced to zero during each pass through the wet oxidation reactor. Rather, what is required is that each pass yield an acceptably low steady-state COD value, i.e., one that will not interfere with bleaching or other unit operations.

The data presented here demonstrate that POMS can act as catalysts for, and/or initiators of, aerobic oxidation of the dissolved organic materials and that a low steady-state COD can be achieved in a continuous process of anaerobic POM delignifation followed by aerobic wet oxidation. The POM-catalyzed wet oxidation step is carried out under conditions of temperature and oxygen pressure (ca. 150 °C and 0.7 MPa) which are significantly less aggressive than those typically required for the treatment of pulp-mill effluents (ca. 200-400 °C, 2–20 MPa) (Foussard et al., 1989).

Erperimental Section

Materials. An unbleached mixed-pine kraft pulp with a kappa number of 34 and a viscosity of 28 mPa·s (see Analytical Methods below) was supplied by Consolidated Papers, Inc., Wisconsin Rapids, WI. Bleaching and wet oxidation studies were performed using sodium salts of the α-Keggin anion α-$[PV_2Mo_{10}O_{40}]^{5-}$. This salt is prepared as an equilibrium mixture of α-NaH_{4-x}-$[PVMo_{11}O_{40}]$, α-$Na_xH_{5-x}[PV_2Mo_{10}O_{40}]$, and α-Na_xH_{6-x}-$[PV_3Mo_9O_{40}]$ in which the divanadium species is favored and where the ratios $x/(4-x)$, $x/(5-x)$, and $x/(6-x)$ are determined by pH (Grate et al., 1992). At the pH values used in this work (near 4) all three anions are in their sodium salt forms, that is, $x = 4$, 5, and 6, respectively. In addition, in the di- and trivanadium anions, positional isomers are present. Henceforth, this mixture of compounds, in which α-$[PV_2Mo_{10}O_{40}]^{5-}$ and its positional isomers dominate and in which all vanadium atoms present are in their highest (d^0, +5) odation state, will be referred to as POM_{ox}. Solutions of this salt mixture in which some or all vanadium atoms present have been reduced by one electron to V^{IV} (d^1, +4) ions, will be referred to as POM_{red}. Deionized water was used as a solvent.

Analytical Methods. See the appendix.

Pulp Delignification. Delignification reactions were carried out in 1 or 2 L stainless steel Parr pressure vessels (Model 4541, Parr Instrument Company, Moline, IL). A custom-made helical stirrer was used to provide adequate stirring of pulp mixtures. The reactor pressure was measured with a pressure gauge, and temperatures were controlled using a Parr controller (Model 4842) equipped with a type "J" thermocouple.

In all experiments, target temperatures and reaction times were 125 °C and 0.5 h. Pulp, at 3% consistency (csc, % solids), was heated in 0.5 M POM_{ox} at pH 4. The pH of the bleaching liquor was adjusted before each bleaching cycle by addition of H_2SO_4 or $NaHCO_3$ as necessary, and the concentration of the POM was adjusted before each bleaching run by addition or evaporation of water.

After loading the reactor with pulp, POM, end water (as needed), it was sealed and purged with purified nitrogen for 15 min. The reactor was then charged with N_2 to 25 psig. The contents were slowly stirred throughout the heating cycle (heated from 25 to 125 °C at a rate of 3 °C/min and held at 125 °C for 0.5 h). The reaction was then quenched by immersing the reactor in a cold water bath for ca. 15 min. The CO_2 from the reactor was collected, and the fibers were separated from the POM solution (bleaching liquor) by vacuum filtration and pressing. The PH, [POM], $[POM_{red}]$, and COD values of the bleach liquor were then determined. The delignifiied pulp fibers were washed with water, dried in air, weighed, and analyzed for kappa number and viscosity.

Wet Osidatiom A. Model Compounds. Stock solutions of model compounds were prepared by dissolving veratryl alcohol (200.3 mg/L) and D-glucose (375.1 mg/L) in purified water. In principle, the COD corresponding to each of these stock solutions was 400 mg of O_2/L. Measured COD values for these solutions were 413 ± 10 mg of O_2/L for D-glucose and either 405 ± 10 or 416 ± 10 mg of O_2/L (two different stock solutions) for veratryl alcohol. Control experiments (without added POM) were performed on the undiluted stock solutions, adjusted to pH 3 by addition of concentrated sulfuric acid. For expeximente using POM_{ox}, solid POM salt (0.048 M) was added to the stock model compound solutions at pH 3 and the final volumes were recorded. Wet oxidation reactions, with and without POW present, were carried out in a Parr reactor, using oxygen partial pressures of 0.7 MPa (100 psig). COD values were determined using the "open reflux method".

B. POM Delignification Liquors. Wet oxidation reaction were carried out in the same reactors as those used for delignification, and a high-speed gas entrainment impeller was used to circulate the reactor head gases through the liquid. In a typical experiment, freshly obtained bleach liquors, without adjustment of pH or [POM], were transferred to the wet oxidation reactor, which was sealed and purged with O_2 for 10 min. The reactor was then charged to 0.7 MPa of O_2, the impeller spun at 1200 rpm, and the reactor heated to 150 °C for 4 h (heated from 25 to 150 °C at a rate of 3 °C/min and held at 150 °C for 4 h). In experiments designed to determine kinetic parameters, the reactor was purged with N_2 prior to heating, end oxygen pressure was applied only after the reactor reached 150 °C ($t = 0$ min). After 4 h at temperature, the reaction was quenched as described above, and the CO_2 was collected. The pH, [POM], $[POM_{red}]$, and COD values of the wet oxidation liquor were then determined.

C. Initial Rate vs Impeller Speed. Wet oxidation was carried out as described above using 400 mL aliquots taken from a single POM bleach liquor (initial COD = 1880 mg of O_2/L). The reactor was purged with N_2 prior to heating, and oxygen pressure was applied only after the reactor reached 150 °C ($t = 0$ min. Samples were taken from the pressurized reactor at $t = 0, 3, 6$, and 9 min via a sampling tube which extended
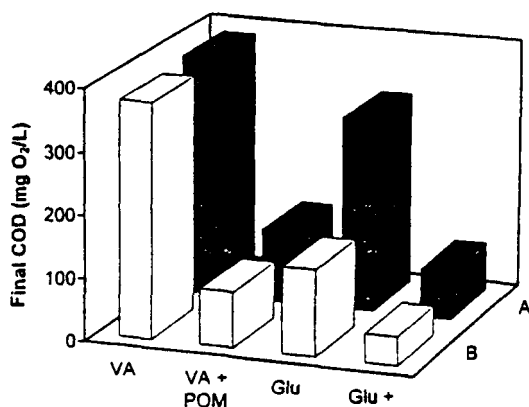
Figure 3. Reduction in the COD values (mg of O_2/L) of standard solutions (400 mg of O_2/L) of veratryl alcohol (1,3-dimethoxybenzyl alcohol, VA), a lignin-fragment model, and of D-glucose (Glu), a Polysaccharide-fragment model, during wet oxidation (0.7 MPa O_2) with and without POM_{ox} (0.046 M). Two temperature profiles were used: (A) 4 h at 150 °C; (B) 2 h at 150 °C followed by 1 h at 200 °C.

Figure 4. COD values (+, mg of O_2/L and extent of reduction of POM (O, % reduction) during the wet oxidation (150 °C, 0.7 MPa O_2, gas entrainment impeller speed of 1200 rpm) of a POM bleach liquor possessing an initial COD of 1650 mg of O_2/L. Oxygen was introduced to the reactor (preheated under a nitrogen atmosphere) at t = 0 min.
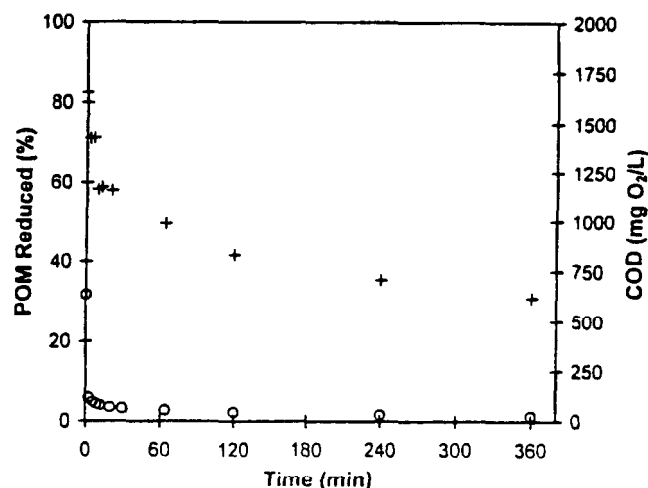
below the liquid level. At each time point, the sample tube was purged with 5 mL of liquor, and then 6-8 mL of sample was collected. To avoid flashing, 30–45 s was required to collect each sample. The COD value was determined for each sample and corrected for the amount of POM_{red} present. Due to the critical nature of the initial COD values, two samples were obtained just prior to t = 0 min in each reaction (the tube was purged between samples). The COD of every sample was determined four times to increase accuracy, and the average values were used to create plots of the COD values versus time. Initial rates of COD decrease were calculated for the first 3 min as - Δ COD units/3 min. Initial rates were determined at several impeller speeds (300, 550, 1000, 1670, and 21.20 rpm) with duplicates at 1000 and 1670 rpm.

Results and Discussion

Wet Oxidation of Model Compounds, The potential effectiveness of POM_{ox} as a catalyst or initiator of wet oxidation reactions was assessed using solutions of model compounds. Veratryl alcohol (1,3-dimethoxybenzyl alcohol) and D-glucose were chosen to represent the lignin and polysaccharide fragments expected to dissolve during bleaching. (Although the purpose of bleaching is to remove lignin, polysaccharide fragments are also likely to be present in the spent liquors.) After 4 h at 150 °C (temperature profile A) under an oxygen pressure of 0.7 MPa (100 psig), the COD values of model compound solutions containing POM are substantially lower than those for the corresponding POM-free controls (Figure 3).

A protocol which consists of shortening of the total reaction time to 3 h, while increasing the temperature to 200 °C in the third hour (temperature profile B), gives results similar to those for temperature profile A. In the absence of POM, the COD values for the lignin model solutions remain largely unchanged. However, when POM is present, the COD values are substantially reduced. Although COD values of the D-glucose solutions are more easily reduced, the presence of POM nonetheless considerably accelerates the reaction. These data clearly establish a catalytic role for POM anions.

Wet Oxidation of a POM Bleach Liquor. In actual bleach liquors, a wide variety of lignin and polysaccharide fragments are likely to be present. The

data for the model studies indicate that POM_{ox} is likely to accelerate the wet oxidation of bleach liquors. Some POM aniona, for example, $\alpha\text{-}[SiVW_{11}O_{40}]^{5-}$, are more effective at delignification than is $\alpha\text{-}[PV_2Mo_{10}O_{40}]^{5-}$ (POM_{ox}); at pH 5 the reduction potential ($E_{1/2}$) of $\alpha\text{-}[SiVW_{11}O_{40}]^{5-}$ is +0.69 V vs a normal hydrogen electrode (NHE), while that for $\alpha\text{-}[PV_2Mo_{10}O_{40}]^{5-}$ at pH 4 is estimated to be near +0.52 V (Weinstock et al., 1996). However, the reduced anion, $\alpha\text{-}[SiVW_{11}O_{40}]^{5-}$, reacts more slowly with O_2 than does $\alpha\text{-}[PV_2Mo_{10}O_{40}]^{6-}$ (POM_{red}) and its potential usefulness in wet oxidation has yet to be determined. In the present study, $\alpha\text{-}[PV_2Mo_{10}O_{40}]^{5-}$ (POW_{ox}) is used for both delignification and wet oxidation. In addition, the conditions used in the bleaching reactions ([POM], time, temperature, pulp consistency) were adjusted to provide for experimentally convenient COD values rather than for optimal delignification.

To obtain a bleach liquor, unbleached kraft pulp (3% consistency, csc) was combined with a 0.5 M solution of POM_{ox} and heated with gentle stirring under nitrogen to 125 °C for 0.5 h at pH 4. During this time, 33% of the POM anions (16.5% of the vanadium present) was reduced to V^{IV} and the lignin content of the pulp decreased from 5.1% to ca. 3.3%. Organic compounds dissolved during bleaching increased the COD value of the solution by 1650 mg of O_2/L.

This liquor was loaded in a Parr reactor fitted with a gas entrainment impeller. The reactor was purged with nitrogen and sealed the impeller was spun at 1200 rpm, and the system was heated. Once the reactor reached 150 °C, a sample wes removed (t = 0 min) and a partial pressure of 0.7 MPa O_2 was applied. The COD of the solution and amount of reduced POM present, $[POM_{red}]$, were measured at regular intervals for 6 h (Figure 4).

After an initial rapid decrease in COD values, the reaction slowed dramatically. During the first few minutes of the reaction, the rate at which the COD decreased was ca. 100 COD units/min. After 4 h, the rate declined to a value of 1 COD unit/min. After 6 h, the COD of the solution was 38% of its initial value. The concentration of reduced POM anions, as indicated by the absorbance of the solution at 710 nm, initially decreased rapidly to a value near zero and thereafter remained low. The nonzero absorbance value can be
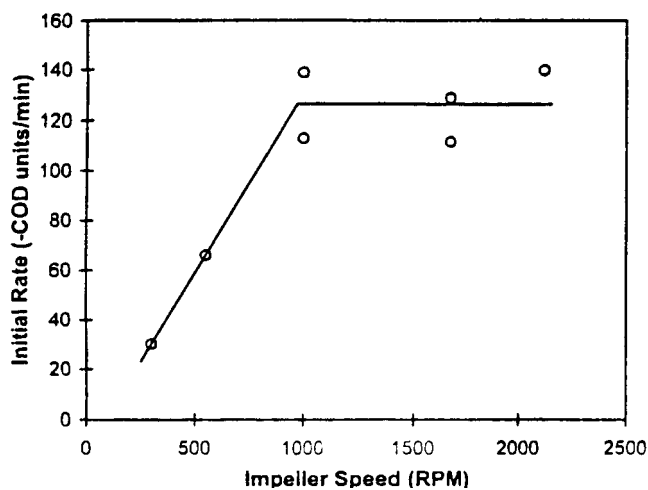
Figure 5. Initial rates (–COD units/min) for the wet oxidation (150 °C, 0.7 MPa O_2) of a POM$_{ox}$ bleach liquor (initial COD = 1880 mg of O_2/L.) at several impeller speeds (rpm). Initial rates at impeller speeds of 1000 and 1670 rpm were determined twice.

attributed to the presence of organic chromophores (the small absorbance of POM$_{ox}$ at 710 nm was subtracted).

Diffusion of Oxygen into POM Solutions. Grate et al. (1992) have reported that solutions of α-[PV$_2$Mo$_{10}$-O$_{40}$]$^{5-}$ can be used to catalyze the aerobic oxidation of Pd^0 to Pd^{II} in the oxidation of ethylene to acetaldehyde (Cataiytica Olefin Oxidation Technology). These authors found that, at 27 psi and 120 °C, the rate of oxidation of 0.3 M solutions of reduced α-Li$_4$H[PV$_2$Mo$_{10}$-O$_{40}$] by oxygen was mass-transfer-limited even at impeller speeds greater than 3000 rpm. Thus, as a prerequisite to further optimization, the role of oxygen difusion in wet oxidation was assessed by measuring the initial rate of the reaction at several impeller speeds.

Initial rates (-dCOD/dt, averaged over the first 3 min) for the wet oxidation of a POM bleach liquor (initial COD = 1880 mg of O_2/L) were measured for impeller speeds ranging from 300 to 2120 rpm (Figure 5). Because of the relatively long times required to obtain samples from the reactor (30-45 s), scatter was observed in the data at higher impeller speeds (i.e., faster initial reaction rates; see the Experimental Section). To compensate, initial rates at impeller speeds of 1000 and 1670 rpm were determined in duplicate.

At rotation rates greater than ca. 1000 rpm, the initial reaction rate is independent of impeller speed. Thus, at 1200 rpm (Figure 4) the rapid phase of the reaction is kinetically, rather than oxygen transfer, limited. The reaction kinetics also control the overall rate in the intermediate and later stages of the reaction. Even in the presence of POM$_{ox}$ and excess dissolved O_2 during the later, slower phases of the reaction, the wet oxidation no longer occurs at an industrially useful rate.

In general, the POM might accelerate the wet oxidation reactions in two inter-related ways: (i) as a catalyst, directly oxidizing organic substrates or (ii) as an initiator of radical-chain autoxidation processes. In order to act in the latter capacity, it must first be reduced by electrons originating in the C-C and C-H bonds of the organic substrate. The electrons present in the reduced POM anions can then be transferred to O_2 molecules, generating a variety of highly active reduced-oxygen species (Duncan and Hill, 1997). The two functions of the POM anion can overlap when radical-chain autoxidation reactions are initiated or propagated by the reaction of organic radicals, generated by the direct oxidation of organic substrates by POM$_{ox}$, with oxygen.

After an initial rapid phase (Figure 4), the reaction slows considerably. It is probable that during the slow phase of the reaction only refractory organic compounds, for which the rates of direct oxidation by POM$_{ox}$ are very low, remain. As a result, direct catalysis by the POM is very slow. At the same time, because initiation of radical processes requires reduction of the POM anions, their ability to initiate radical-chain processes is likewise compromised.

To overcome this difficulty without resorting to higher temperatures, which would dictate more expensive reactors and higher energy costs, one could introduce a more readily available source of electrons for the reduction of the POM$_{ox}$ anions. One way to accomplish this introduction would be to add untreated lignin and polysaccharide fragments to the wet oxidation reactor after completion of the initial rapid reaction phase. Such additions are a natural consequence of converting the current process to a continuous mode of operation.

After the rapid phase of wet oxidation is completed, the POM liquor, now containing POM$_{ox}$ and a variety of refractory organic materials, is returned to the bleaching reactor. Because this unit operation is carried out anaerobically and at a lower temperature than that used for wet oxidation, the refractory organic compounds are unlikely to interfere with the bleaching process. After bleaching, the POM$_{red}$ liquor will contain the refractory compounds carried over from the previous wet oxidation step and, importantly, freshly dissolved lignin and polysaccharide fragments. Upon initiation of wet oxidation, these fragments, as well as the reduced POM anions themselves, can supply the electrons necessary for the initiation of radicak-chain autoxidation processes. These reactions are likely to convert some additional portion of the refractory compounds to carbon dioxide and water. Thus, after a period of continuous operation, it is conceivable that the system might reach a steady-state COD level which is acceptably low.

Achievement of a Steady-State COD Value after Repeated Cycles of Bleaching and Wet Oxidation. A series of cyclical batch delignification and wet oxidation reactions was carried out to investigate the possibility of obtaining a quasi-steady-state COD level. Although it would have been preferable to study a continuous-reactor system, acquisition and optimization of the laboratory-scale equipment necessary for pumping high-solids pulp slurries in such a closed system would have been prohibitively expensive and time consuming.

Experimental conditions and analytical data for the delignification and wet oxidation reactions are given in Tables 1 and 2. The entire series of reaction cycles was carried out using a single POM liquor.

The [POM] in the liquor was maintained at 0.5 M by evaporation or addition of water after each bleaching/wet oxidation cycle; no additional POM$_{ox}$ was added. After each bleaching reaction, the pulp was pressed to remove most of the POM solution present. To avoid large variation in the concentrations of the POM in the liquor, pulp-washing streams were not added back to the system. Thus, the volume of the POM liquor decreased with every bleaching cycle (Table 2). In principle, the combination of delignification followed by wet oxidation should have no net effect on the pH of the POM liquor (Figure 2). In general, this expectation was borne out in the present experiment. However, in order to minimize random variations and to compensate for alkali brought into the system with the pulp itself,

Table 1. Reaction Condition and Analytical Data for the Anaerobic POM$_{ox}$Delignification of Unbleached Wood Pulp (See Text)

cycle	1	2	3	4	5	6	7	8	9
reaction temp (°C)	150	128	126	127	126	126	200	127	127
time (h)	0.5	0.5	0.5	0.5	0.5	0.5	b	0.5	0.5
[POM] in	0.50	0.50	0.50	0.50	0.48	0.50	0.48	0.48	0.45
[POM] out	0.47	0.49	0.50	0.49	0.47	0.49	0.47	0.47	0.44
pH in	3.80	3.95	3.94	4.02	3.87	3.89	3.91	3.92	3.60
pH out	a	a	3.96	4.06	4.10	3.97	3.34	3.97	3.78
kappa in	34	34	34	34	34	34	34	34	34
kappa out	20	23	23	19	21	21	13	22	23
viscosity (mPa·s)	11	15	18	17	18	24	4	18	18
[POM]$_{red}$	0.028	0.023	0.033	0.042	0.043	0.034	0.164	0.039	0.038
pulp in (g)	54.1	43.6	34.1	28.1	24.6	19.0	15.5	12.1	10.0
pulp out (g)	49.2	41.4	31.6	26.7	23.1	18.9	13.0	10.3	9.6
volume of POM solution (mL)	1750	1409	1103	909	796	615	501	390	323

^{a} Data not available. ^{b} Reactor was cooled to 25 °C immediately after reaching 200 °C.

Table 2. Reaction Conditions and Analytical Data for the Wet Oxidation of POM Bleaching Liquors (See Text)

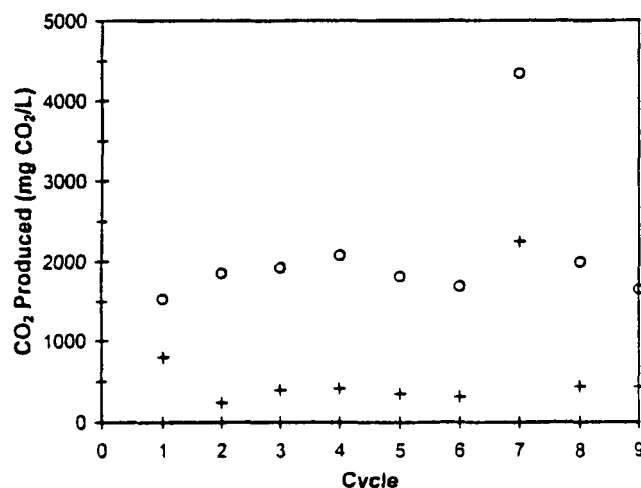| cycle	1	2	3	4	5	6	7	8	9
reaction temp (°C)	150	150	150	150	150	150	150	150	150
time (h)	4	4	4	4	4	4	4	4	4
[POM] in	0.47	0.49	0.47	0.45	0.44	0.45	0.42	0.41	0.37
[POM] out	0.48	0.48	0.48	0.46	0.44	0.45	0.43	0.43	0.38
pH in	a	a	3.96	4.06	4.10	3.97	3.34	3.97	3.78
pH out	3.95	3.60	4.06	4.05	4.26	4.04	4.15	4.20	4.09

^{a} Data not available.
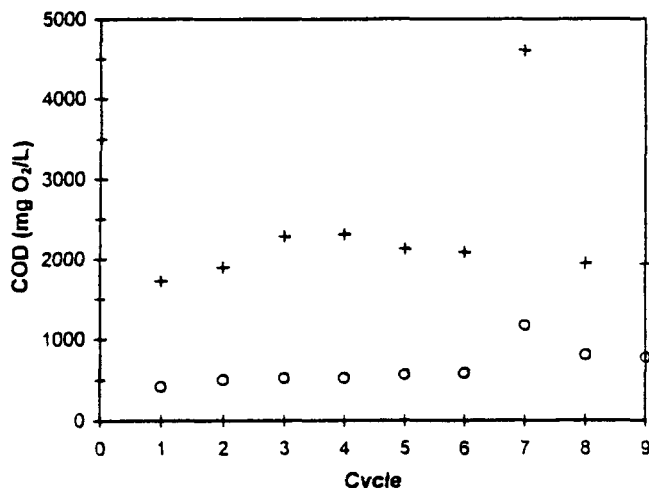
Figure 6. COD values of a single POM solution used in nine cycles of anaerobic bleaching (0.5 h at 125 °C, 0.50 M POM$_{ox}$) followed by wet oxidation (4 h at 150 °C, 0.7 MPa O$_2$, impeller speed of 1200 rpm): (+) after bleaching (O) after wet oxidation.

Figure 7. Carbon dioxide collected from reactors used in nine cycles of anaerobic bleaching (0.5 h at 125 °C, 0.50 M POW$_{ox}$ followed by wet oxidation (4 h at 150 °C, 0.7 MPa O$_2$, impeller speed of 1200 rpm); (+) after bleaching (O) after wet oxidation.

the pH of the POM liquor was adjusted to near 4.0 just prior to each delignification reaction by addition of small amounts of H$_2$SO$_4$ or NaHCO$_3$. After each delignification or wet oxidation reaction, the COD values of the POM liquors and the carbon dioxide generated were determined (Figures 6 and 7).

After the first bleaching reaction (cycle 1, Figure 6), the COD of the bleach liquor was 1723 mg of O$_2$/L. The open circle plotted for this cycle (421 mg of O$_2$/L) identifies the COD value of this liquor after the subsequent wet oxidation step. After two cycles, the COD of the liquor leaving the wet oxidation reactor appears to have reached a stable value. The amount of CO$_2$ generated during wet oxidation (Figure 7) also appears to level off after two to three cycles.

The steady state was maintained until cycle 7, during which incorrect placement of a thermocouple led to a rise in the temperature of the bleaching reactor to 200 °C. At the end of this bleaching step, the COD of the liquor was 4609 mg of O$_2$/L. Although unplanned, this

event provides insight into the ability of the system to tolerate excursions. After wet oxidation, carried out exactly as previously described, the COD (1171 mg of O$_2$/L; cycle 7, open circle) was twice the earlier established steady-state value. However, in cycles 8 and 9, the COD returned to near its previous level. (One caution, here, is that the COD increases that resulted from the bleaching steps of cycles 8 and 9 were somewhat low. Inspection of the bleaching reaction data in Table 1, however, reveals no significant differences between these cycles and those of previous cycles. Moreover, the ^{31}P NMR spectra of the POM bleaching liquor, diagnostic for the presence and state of POM$_{ox}$, showed no changes over all nine cycles.)

In the first bleaching reaction (cycle 1, Figure 6), 1723 mg of O$_2$/L of organic compounds was added to the POM liquor. The COD of these compounds was reduced to 421 mg of O$_2$/L during the first wet oxidation reaction in the series. This decrease (76%) is consistent with the 62% decrease observed after 6 h in the batch experiment
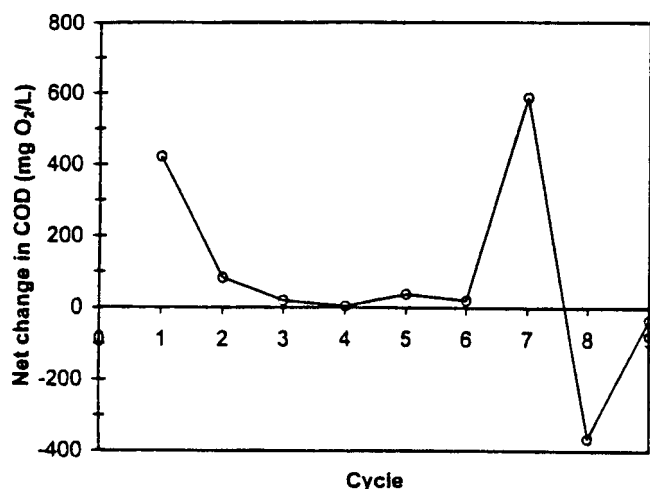
Figure 8. Net changes in COD values (mg of O_2/L) of the POM liquor (data from Figure 6) after each full cycle of bleaching followed by wet oxidation.

described earlier (Figure 4). (Note that, in the earlier case, the reactor was heated to temperature under anaerobic conditions.) In addition, the organic compounds that remained after 4 h (Figure 4) were relatively refractory, such that the rate of COD decrease in the slow phase was very low (ca. 1 COD unit/min). On the basis of these observations, one might have expected the COD values measured after each cycle in the present experiment to increase steadily. That is, anticipated per-cycle COD increases might have been expected to equal about 24% of the COD of the organic material added in each bleaching step. Instead, after two cycles, the net increases in COD per cycle drop to near zero (Figure 8).

These results provide strong evidence for synergistic enhancement of the rate of COD reduction and signals the achievement of a quasi-steady-state condition. Achievement of this state implies the overall conversion of dissolved organic compounds to carbon dioxide and water, a necessary condition for effluent-free operation. Preliminary data demonstrating an analogous result, obtained in an eight-cycle experiment, have been reported (Weinetock et al., 1997). There a 0.05 M POM solution was used and the COD increase in each bleaching step was ca. 500 mg of O_2/L. A steady state was observed after four or five cycles. The steady-state COD value (ca. 550 mg of O_2/L) was indistinguishable from that observed here.

The model compound studies (Figure 3) clearly indicate that the POM anions, α-[$PV_2Mo_{10}O_{40}$]$^{5-}$ and α-[$PV_2Mo_{10}O_{40}$]$^{6-}$, accelerate the wet oxidation reactions. Thus, the rapid achievement of a steady-state COD condition can be attributed to both the POM acceleration of the wet oxidation reactions in general and POM augmentation of synergistic enhancement (Willms et al., 1987). The precise role of the POM anions is being investigated using simple organic compounds as models for dissolved lignin and polysaccharide fragments. In addition, the effects of key variables are the subject of ongoing work. Also, the development of POM anions optimized for maximal effectiveness in both selective delignification and catalytic wet oxidation is in progress.

Conclusions

The polyoxometalate (POM) anion, α-[$PV_2Mo_{10}O_{40}$]$^{5-}$, is used both as a direct oxidant of lignin in anaerobic delignification (bleaching) of wood-pulp fibers and,

subsequently, as a catalyst for aerobic conversion of the dissolved lignin to carbon dioxide and water. Although single 4 h residence times in the wet oxidation reactor decrease the COD values of the POM stream by only ca. 75%, a low steady-state COD value is achieved after only a few cycles of bleaching and wet oxidation. The rate of the wet oxidation reactions is accelerated by the POM anions, which can catalyze the oxidation of organic compounds directly and/or act as initiators for radical-chain autoxidation processes. Moreover, freshly dissolved organic compounds are added during each bleaching step. These act as a source of electrons for the activation of dioxygen, which leads to further conversion of refractory organic compounds (synergistic enhancement). Together, the processes described and demonstrated here could provide the basis for the development of new, oxygen-based and effluent-free, delignification processes, including both pulping and bleaching. At the same time, the present demonstration of a steady-state condition suggests that synergistic enhancement might be used to advantage in industrial wet oxidation processes wherein the formation of refractory compounds is rate limiting.

Appendix: Analytical Methods

A. Pulp Properties. The kappa number of a wood pulp is a standard pulp and paper industry index of its lignin content. Kappa numbers are determined by measuring the extent to which a standardized solution of permanganate is reduced when mixed with a pulp sample at a given temperature for a given time. Weight percent lignin in pulp is empirically determined to be $0.15 \times$ kappa number. Kappa numbers of unbleached kraft pulps vary from approximately 20 to 35 (3.00-5.25% lignin). Microkappa numbers (obtained from relatively small pulp samples) were determined using the Technical Association of the Pulp and Paper Industry (TAPPI) useful method um-248 (TAPPI, 1991a). The terms kappa number and microkappa number are used interchangeably.

Pulp viscosity, a nonlinear function of the degree of polymerization of the cellulosic component, is an indirect measure of the extent to which fibers have been damaged by degradation of individual cellulose chains. Higher viscosity pulps generally result in paper products with higher tensile strengths. Viscosity measurements were obtained, using a capillary viscometer, from solutions of pulp samples in aqueous solutions of ethylenediamine and cupric sulfate (TAPPI test method T230 om-89) (TAPPI, 1991b). Viscosities of unbleached kraft pulps are generally near 30 mPa·s, and those of market-grade bleached pulps range from roughly 15 to 25 mPa·s.

B. NMR of POM Solutions. Routine ^{31}P and ^{51}V NMR spectra were obtained with a 250-MHz Bruker instrument according to published methods and externally referenced to H_3PO_4 and $VOCl_3$, respectively (Leparulo-Loftus and Pope, 1987).

C. Concentration of POM. The molar concentration of the POM salt (α-Na_5[$PV_2Mo_{10}O_{40}$]) was taken as half the total concentration of vanadium. Vanadium concentrations were determined by mixing known volumes (typically 5-10 mL aliquote diluted 10-fold) of POM solutions with equal volumes of concentrated H_2SO_4 and titrating with a standardized solution of ferrous ammonium sulfate (FAS) to ferroin (1,10-phenanthroline ferrous sulfate) endpoints. In the case of POM$_{red}$ solutions, several drops of Br_2 were added before addi-

tion of acid to oxidize the vanadium to V^V, and the excess bromine was removed by thoroughly purging with air.

D. Extent of Reduction of POM$_{red}$ Solutions. Molar concentrations of the reduced POM salt (as α-Na$_6$[PV$_2$Mo$_{10}$O$_{40}$], i.e., one V^{IV} atom per divanadium anion) were determined spectrophotometrically at 710 nm (ϵ = 875). Calibration data were obtained by titrating 0.1 mL of a ca. 0.5 M POM solution, diluted to 10 mL with dilute (pH 1) aqueous H$_2$SO$_4$, with 0.001 N ceric sulfate acidified to pH 1 using H$_2$SO$_4$.

E. Chemical oxygen Demand (COD). COD measurements (in units of mg of O$_2$/L) were used to quantify the concentrations of dissolved organic species in bleaching and wet oxidation liquors. Two different methods for determining these values were used. The first is a modification of the "open reflux method" (American Public Health Association, 1985). This method entails the exhaustive oxidation of organic compounds in aqueous solution. The solution being tested is mixed with concentrated H$_2$SO$_4$, along with an excess of potassium dichromate, and the combination is heated to reflux (ca. 150 °C) for several hours. The extent of reduction of the dichromate is then determined by titration with ferrous ammonium sulfate (FAS) using a ferroin indicator.

For solutions containing POM salts, the endpoint was obscured and had to be determined spectroscopically. As FAS is added, unreacted dichromate is reduced first, followed by the oxidized V^V species. Reduction of vanadium is observed as an increase in the absorbance at 760 nm. Absorbance at this wavelength is monitored during FAS addition, and the endpoint is defined as the point where reduction of vanadium first begins. Absorbance values were corrected for the volumes of titrant added.

A second dichromate method, the "closed reflux method" (American Public Health Association, 1985) is more convenient and is approved by the Environmental Protection Agency (EPA 1978). Premade kite were purchased from Bioscience, Inc., Bethlehem, PA (Bioscience Inc., 1993). In this method, COD values are obtained by spectrophotometric determination of the concentration of reduced chromium ions (Cr^{III}, λ_{max} 600 nm). To avoid complications associated with the presence of V^V species, which absorb strongly below 600 nm but only weakly at longer wavelengths, 630 nm was chosen for quantitation of Cr^{III} ions. Extinction coefficients were determined using standard solutions. Concentrations of reduced POM were determined prior to reaction with dichromate and subtracted from final COD values.

In principle, the COD is the mass of oxygen required to completely oxidize all organic compounds in the test sample to CO$_2$ and H$_2$O. In practice, it is a measure of the degree to which the dichromate is reduced under the conditions of the test. In POM bleaching liquors, mixtures of both lignin and polysaccharide fragments are present. The dissolved lignin fragments are hydroxylated and methoxylated phenylpropane derivatives possessing α-alcohol, α-ketone, and α-acid substituents. These fragments, along with simpler aliphatic alcohols and organic acids that may be present, are quantitatively, or nearly quantitatively, oxidized to CO$_2$ and H$_2$O during the COD test (Dobbs and Williams, 1963). In addition, cellulose and other polysaccharides are rapidly hydrolyzed in hot aqueous sulfuric acid to glucose end other simple sugars, all of which are completely oxidized

by the acid bichromate solution to CO$_2$ and H$_2$O (Moore et al., 1949). In the present work both D-glucose and 1,3-dimethoxybenzyl alcohol (veratryl alcohol, an aromatic model for dissolved lignin fragments) were completely oxidized to carbon dioxide and water during the COD test.

F. Carbon Dioxide Produced. After each bleaching or wet oxidation reaction, the head gases from cooled reactors were released through a series of three columns (60 × 2.5, 60 × 2.5, and 30 × 2.5 cm), containing 0.10-0.25 N aqueous solutions of Ba(OH)$_2$. In the third column, the inlet was fitted with a glass frit to improve gas-liquid contact and several drops of isopropyl alcohol were added as a surfactant to decrease the gas-bubble size. Carbon dioxide reacts with Ba(OH)$_2$ according to eq 2. Barium concentrations were adjusted to ensure the presence of 100% molar excesses of this species.

$$CO_2 + Ba(OH)_2 \rightarrow BaCO_{3(ppt)} + H_2O \qquad (2)$$
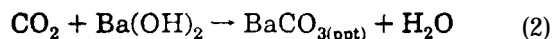
Once the reactor pressure reached atmospheric, purified nitrogen was forced through the reactor headspace (not bubbled through solution) for 15 min to ensure collection of all the head gas. The solutions from the three columns were then combined and titrated with 0.25 N HCl to a phenolphthalein endpoint.

A series of experiments was performed to develop an empirical model for determining the amount of CO$_2$ remaining in solution. Sodium carbonate end H$_2$SO$_4$ were injected into 0.5 M POM solutions in the reactor. The reactor was heated and cooled as in the wet oxidation experiments and the CO$_2$ collected as described above. Repetitions of this experiment at three different liquid volumes provided an empirical calibration curve for estimating the total fraction of CO$_2$ collected. Reported CO$_2$ values have been adjusted accordingly.

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