

CLOSED-MILL DELIGNIFICATION BY DESIGN USING POLYOXOMETALATES

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ABSTRACT

Polyoxometalates (POMs) are a class of delignification agents that promise to provide the basis for a new closed-mill bleaching technology. The results presented here are based on the use of $\text{Na}_6\text{SiV}_2\text{W}_{10}\text{O}_{40}$, which is effective in reducing the Kappa number of softwood Kraft pulp from 30 to below 10 with minimal loss in viscosity. A critical part of a viable POM process is the elimination of the organic lignin and carbohydrate-derived fragments dissolved during the delignification. To simulate a closed process, a series of pulp samples were delignified with the same POM liquor. Before each pulp sample was treated, the liquor was oxidized to regenerate the POM and remove a large portion of the organic material dissolved during the previous delignification step. By collecting and reusing the wash water during this set of experiments, we showed that a steady-state carbon load will be achieved and that the proposed industrial process is feasible. The rate of the wet oxidation of organic material was similar to the rate observed for acetate oxidation

INTRODUCTION

During the past five years, a new delignification system, based on the use of polyoxometalates (POMs) as regenerable oxidants, has been under development at the USDA Forest Service, Forest Products Laboratory (FPL), in Madison, Wisconsin [1-14]. The POMs are transition-metal-substituted cluster anions. When applied in their active states, they can selectively oxidize lignin and related chromophores, leaving the cellulose largely undamaged. The attractiveness of POMs as delignification agents is enhanced by the fact that they can be reactivated with oxygen under conditions that can catalyze oxidation of the solubilized organic products of the delignification process. Thus; they can be continuously recycled in a closed system. This technology promises to provide the basis for a new class of closed bleach plants in which the only consumable oxidant is oxygen and the primary by-products are carbon dioxide and water.

In this study, we developed an experimental system that is a model of a continuous POM delignification process using batch operation of laboratory equipment. The goals included the establishment of a steady-state level in the liquors with regard to the organic content; verification of the carbon balance of the system based upon pulp delignification, yield, CO_2 and volatile organic compounds (VOCs); and confirmation of POM stability, buffering capacity and effectiveness. With these data we were able to confirm that the POM process can meet the goal of being closed with respect to liquid effluents.

Background

Discovery of the delignifying action of POMs occurred in the context of a new program on alternative pulping and bleaching. Studies of wood-degrading fungi [15] showed that the peroxidase enzyme systems are highly selective. They attack the aromatic constituents of the cell wall and leave the cellulose intact. Later, a system of hydrolases is released by the fungi that converts cellulose to glucose, which is then directly assimilated as a nutrient-

It has been recognized that the selectivity of the peroxidases is based on the activity of transition-metal ions that function as electron shuttles during the oxidation of lignin. Indeed, there is considerable literature [16] on organic peroxidase analogs that are effective in the oxidation of lignin. These systems require porphyrins, complex organic platforms, to control the coordination of the transition-metal ions. Since porphyrins are costly to produce and are not stable at the temperatures necessary to achieve industrially feasible rates, they remain largely of academic interest.

A major breakthrough in our program occurred when we recognized that polyoxometalate cluster anions could provide a structure that mimics the function of porphyrins in fungal enzyme systems. The POMs are a class of oligomeric, metal-ion oxide clusters. The ones used in our program typically include 12 structural transition-metal atoms, such as tungsten or molybdenum, clustered around a main-group atom, such as phosphorus, silicon, or aluminum. To make them active for delignification, we replace one or two of the structural metal atoms of the cluster ion with a redox-active first-row transition-metal atom, such as vanadium or manganese.

Process Concept

To favor high selectivity during delignification, POMS will be applied to the pulp under anaerobic conditions. If oxygen is present, free radicals are produced that can react unselectively with cellulose, which results in inferior pulp strength properties. In fact, these unselective reactions are used to mineralize the lignin fragments dissolved in the liquor during delignification. When the spent bleaching liquor is exposed to oxygen at elevated temperatures, the POM is reoxidized to its active form and free-radical species are generated. Under these conditions much of the organic material is oxidized to carbon dioxide and water, but the POMs are unaffected since the structural metal ions in the clusters are in their highest oxidation states. After reoxidation the POM solution can be used to delignify pulp again.

The process as presently envisioned is shown in Figure 1. The key unit operations are the bleaching stage (A) and the wet oxidation stage (D).

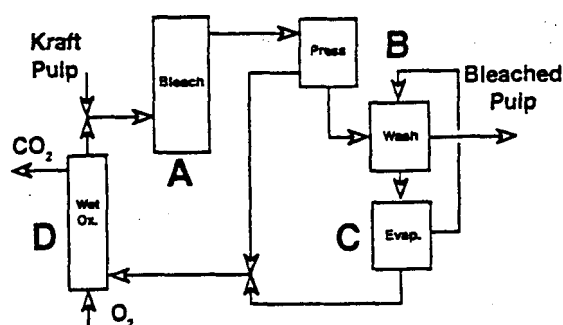


Figure 1. Block diagram of the POM process.

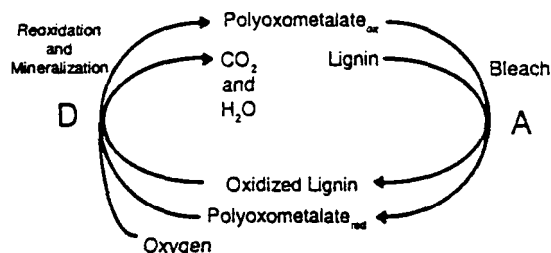


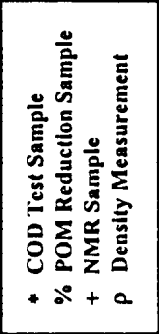
Figure 2. Net reactions of the POM process.

A commercial installation will also require separating the pulp from the bleaching liquors, washing the pulp, and concentrating the wash waters to recover the POM removed during washing. It is anticipated that a stage for removal of non-process elements will be incorporated into the overall scheme. Since a number of preliminary studies have demonstrated that washing with adequate recovery can be accomplished using established technologies, the focus of our program has been on improving the bleaching and wet oxidation stages. We are also seeking a deeper fundamental understanding of the physical and chemical processes that dominate each of the two stages.

The overall chemical processes occurring in unit operations A and D are represented in Figure 2. The bleaching operation (A) is represented as the combination of the POM in its oxidized forms with the lignin to produce the soluble oxidized lignin and the POM in its reduced form. The solubilized oxidized lignin, together with the reduced POM, is then fed into the reoxidation stage, where the POM is reoxidized and the solubilized lignin is mineralized.

EXPERIMENTAL

Figure 3 shows the experimental unit operations for one complete delignification/wet oxidation cycle. In this diagram Pred and Pox stand for reduced and oxidized POM, respectively. To aid in navigation, heavy lines indicate the flow path of the majority of the POM liquor. The pulp enters the system at the "Bleach" unit operation and, after passing through "Press" and "Wash A," exits the system at "Wash B."



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In order to evaluate the environmental impact of the POM process, the collection of VOCs was given a high priority. This resulted in a rather complex experimental system, as illustrated in Figure 3. The wash liquors are recovered for use in the subsequent cycle with different fractions of condensate, containing various VOC concentrations, being returned to the process.

Many measurements were taken during the course of the study. The chemical oxygen demand (COD) of the bleaching liquors, wet oxidation liquors, VOC-laden condensates, and wash waters was measured Using $\text{Ba}(\text{OH})_2$ solutions, the CO_2 production for each reaction was determined titrimetrically. Dissolved CO_2 was determined by refluxing and collecting the evolved CO_2 . The amount of reduced POM and the pH were monitored throughout the system. The pulp was analyzed for yield, extent of delignification and viscosity. The stability of the POM was monitored using ^{51}V NMR. The specific tests performed to measure these experimental variables are described in the following text.

Bleaching

The bleaching was done using $\text{Na}_6[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$ at 150°C for 3 hours on a softwood Kraft pulp (Kappa number=32.9 and viscosity=30.4 mPa·s) at 3% consistency. The initial volume of the pulp slurry was 1.5 L. The reaction was carried out in a 2-L Parr reactor equipped with a tapering helical stirrer. The pulp slurry volume decreased slowly over the course of the experiment as liquor samples were taken after each stage for analysis. Samples of pulp for yield calculations were taken prior to and after bleaching. The pulp was mixed thoroughly with the POM solution using a counter-rotating mixer with care taken to avoid any air entrainment. The reactor was purged thoroughly and pressurized to 0.3 MPa with N_2 prior to the heating cycle. The heating ramp took 45 minutes to achieve the reaction temperature. Upon completion, the reaction was quenched by placing the reactor in a cold water bath and allowing it to cool for 15 minutes.

For measurement of the CO_2 produced during bleaching, the reactor pressure was increased to 1.0 MPa with N_2 and the headspace was released to atmospheric pressure into an evacuated 40-L gas-sampling bag. The reactor was pressurized again to 1.0 MPa with N_2 and blown down to atmospheric pressure while the gas was collected in the same bag. Gas law calculations were used to show that over 99% of the CO_2 in the reactor head gas was collected by this method.

Pulp Washing and Wash Water Recovery

The pulp from the bleaching reaction was filtered and pressed to 25% csc. The bulk of the remaining POM was removed in Wash A (Figure 3). The pulp was combined with the concentrated wash liquor from Wash B of the previous stage to give a slurry of 3% csc. This slurry was filtered and the filtrate combined with the pressed bleaching liquor for an overall POM recovery greater than 99%. The POM liquor was then analyzed for dissolved CO_2 . The pulp was washed four additional times, indicated as Wash B in Figure 3, using condensate collected from the previous washing cycle.

Since the wash liquor from Wash B contained trace amounts of POM salts, it was concentrated to about 0.5 L. This wash liquor was diluted to about 1.5 L using condensates containing moderate VOC levels, specifically, the first 10% of the distillate from the distillation of Wash B and the second fractions from the concentration of the bleaching and wet oxidation liquors. This dilute solution of POM and VOCs was used in Wash A of the next cycle.

The bulk of condensate collected from the concentration of the wash liquor from Wash B was combined with the third fraction of condensate from the concentration of POM liquor after the bleaching reaction. This liquor was used in Wash B of the next washing cycle.

Since the amounts of water entering and leaving the system with the pulp were not equal and since POM samples were removed from the system for analysis, the liquid volume was adjusted between each cycle as needed. Any water removed was taken from the last fraction of condensate collected from the concentration of wash water used in Wash B. This liquid contained virtually no COD. Any water added to the system was Millipore filtered water that, by definition (from its use as a test blank), has a COD of 0.0.

Liquor Concentration

The bulk of the POM liquor needed to be concentrated prior to delignification and wet oxidation. Since the first washing filtrate was combined with the bulk of the bleaching liquor, it needed to be concentrated to 0.5 M POM prior to the wet oxidation reaction. In addition, some water entered the system with the pulp, the wet oxidation liquor was further concentrated so that the bleaching reaction was carried out at 0.5 M. However, prior to their concentration, the POM liquors were refluxed in order to collect and measure the dissolved CO_2 . Some VOCs were released during this process, but they were collected and returned to the POM liquor prior to wet oxidation.

Because it was necessary to return the VOCs in more concentrated solutions, the evaporation of water from the liquors was done in three stages for the bleaching liquor and two stages for the wet oxidation liquor. In both cases, the liquor was initially concentrated by 10% (0.25 L from the bleach liquor and 0.10 L from the wet oxidation liquor). The condensate from this evaporation was returned to the POM liquor. This initial condensate, combined with the VOCs scrubbed out of the reflux CO_2 stream (0.05 L), contained about 75% of the VOCs. The COD of this stream was determined prior to returning the VOCs to the POM liquor.

The second fraction of condensate from the evaporation of the POM liquor (0.5 L from the bleach liquor and 0.2 L from the wet oxidation liquor) contained significantly less VOCs (25%). This fraction was collected and combined with concentrated liquor from wash B for use in wash A of the next cycle. The final fraction collected from the bleach liquor (about 1 L) contained virtually no VOCs and was combined with the majority of wash water condensate for use in wash B of the next cycle.

Wet Oxidation

The wet oxidation was done at 210°C for 3 hours at 2.0 MPa O_2 . The initial liquor volume was 1.5 L. The reaction was carried out in a 2-L Parr reactor equipped with a gas entrainment impeller. The reactor was purged thoroughly with N_2 prior to the heating cycle. The heating ramp generally took about 60 minutes to achieve the set reaction temperature. The reaction time began once the reactor reached the set temperature and the oxygen was added. Upon completion, the reaction was quenched by placing the reactor in a cold water bath and allowed to cool for 15 minutes.

For measurement of CO_2 produced during wet oxidation, the headspace of the cooled reactor was released to atmospheric pressure into an evacuated 40-L gas-sampling bag. During the purging of the headspace, the reactor impeller was spun to encourage nucleation of bubbles in the liquor, which was supersaturated with dissolved gases. The reactor was pressurized to 1.0 MPa with N_2 and released again to atmospheric pressure with the gas collected in the same bag.

Measurement of CO_2

To measure the amount of CO_2 collected from reactor head gases, the gas from the sample bag was slowly drawn through a standardized $\text{Ba}(\text{OH})_2$ solution using vacuum. The excess $\text{Ba}(\text{OH})_2$ was titrated with HCl, phenolphthalein endpoint, to determine the amount of CO_2 collected from the reactor and was reported as mg CO_2/L of POM solution.

In order to measure the CO_2 dissolved in the POM liquors, the solution was transferred to a round-bottom flask equipped with a sidearm and 500-mm reflux condenser. The top of the reflux condenser was connected to a scrubber for collecting VOCs. The scrubber was a large test tube filled with 0.05 L of 0°C water, and it was equipped with a gas dispersion tube with 40-70 μm pores. The scrubber was then connected to a 25 x 1000 mm column filled with a standardized $\text{Ba}(\text{OH})_2$ solution. This column was equipped with a bubbling tube. Nitrogen was passed through the system at approximately 0.1 L/min, which collected any VOCs in the scrubber and any CO_2 in the $\text{Ba}(\text{OH})_2$ solution by precipitating BaCO_3 . The POM liquor was brought to a gentle boil and maintained under reflux for 1 hour. The $\text{Ba}(\text{OH})_2$ was titrated as described above. Experiments have demonstrated that the amount of CO_2 retained in the VOC scrubber was below detectable limits. The scrubbed VOCs were combined with the first fraction of VOC-laden distillate from the concentration of POM liquor-

Measurement of COD

The COD of the liquors was monitored at several points in the experimental system. COD vials were obtained from Bioscience and were calibrated using standard solutions of potassium hydrogen phthalate. After the vials were heated to 150°C for two hours, the concentration of reduced chromium was determined spectrophotometrically. The COD values reported here have been corrected for the reduction due to the oxidation of any reduced POM in the liquor. As the sampling of POM liquors was the greatest source of POM loss, only two samples were taken, after the liquor was pressed from the pulp and after the wet oxidation reaction. COD was measured for the VOC-laden condensate, which was recombined with the POM liquors, the wash water, and any water removed from the system.

Miscellaneous Measurements

The amount of reduced POM was measured at several points in the experimental system: prior to and after bleaching as well as prior to and after wet oxidation. The concentration of reduced POM was determined using $\text{Na}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]$ in sulfate buffer at pH 2. Known quantities of solutions were mixed and the absorbance measured at 625 nm to determine the concentration of $\text{Na}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]$ (molar absorptivity of 219 L/mol·cm).

The concentration of the POM liquors was kept as close to 0.5 M as possible for the bleaching and wet oxidation reactions by monitoring the density of the solution. The density of the solution was empirically determined to be linearly related to the concentration according to $[\text{M}] = (\text{density} - 1) \cdot 0.432$, where $[\text{M}]$ is the concentration of POM in mol/L and density is measured at 23°C in g/cm³.

The yield of the pulp was measured by oven drying known amount of the pulp before and after bleaching. Microkappa and viscosity were measured according to TAPPI standard methods, um-246, T230. Samples of the liquors were taken after each bleaching and wet oxidation stage for ⁵¹V NMR analysis to confirm POM stability.

The amount of carbon monoxide in head gases was determined by filling an evacuated 10-cm gas IR cell with a sample of the head gases and acquiring the FTIR spectrum on a Galaxy series FTIR 5000. The peaks at 2170 and 2117 cm⁻¹ in the spectrum were used to estimate the concentration.

RESULTS

Table 1 shows some of the analytical data for 20 cycles of delignification and wet oxidation. Although the pH values are not shown in this table, the pH for all solutions was between 8.4 and 9.5. Inspection of the Kappa values in Table 1 indicates that the POM delignification retained its effectiveness over the entire 20 cycles. The improvement in delignification efficiency as the experiment progressed was caused by changes in reactor geometry as volume decreased. This was confirmed by experiments with fresh POM at the volume of cycle 20 which gave a similar final Kappa number near 5.0. NMR spectra of the POM liquor showed no change in the concentration of the various inorganic species after cycle 2.

The COD of the POM liquors is shown in Figure 4. The data labeled as wet oxidation COD refer to the liquor that was collected after the wet oxidation step, and likewise, the data labeled as bleaching were obtained from the liquor after pressing the pulp. The error bars in this figure represent the 95% confidence interval for the COD measurement and do not indicate the error that would be found upon replicating this set of experiments. As the experiment progressed, the level of organic material increased, but these data do show some curvature, which would suggest approach to an asymptote.

Table 1: Analytical data for the POM delignification cycles.

Cycle	Liquor L	Delignification			Pulp Properties			Wet Oxidation			Total CO ₂ mg CO ₂ /L
		Liquor COD mg O ₂ /L	VOC COD mg O ₂ /L	POM Red. %	Kappa	Visc. mPa s	Yield %	Liquor COD mg O ₂ /L	VOC COD mg O ₂ /L	POM Red. %	
1	1.50	912	101	27.6	9.6	19.3	96.7	230	75	6.4	2810
2	1.45	1126	143	32.7	10.8	22.0	95.9	375	96	6.4	2376
3	1.43	1183	153	33.6	10.9	21.6	95.9	493	101	5.4	2481
4	1.40	1197	171	28.1	10.1	21.0	97.3	685	140	5.8	2694
5	1.37	1511	232	30.6	10.0	20.7	93.0	819	151	5.6	2561
6	1.35	1770	265	30.7	9.4	19.9	93.5	833	206	5.5	2773
7	1.32	1619	319	30.9	9.8	20.7	93.8	991	209	5.5	2344
8	1.32	1841	333	31.9	9.3	20.6	94.8	1022	235	5.2	2592
9	1.29	1768	312	32.3	9.4	21.2	93.1	1154	216	4.8	2578
10	1.27	2108	303	32.2	8.7	20.7	96.4	1149	231	4.5	2897
11	1.24	2066	325	32.5	8.6	20.7	94.9	1266	—	4.5	2675
12	1.23	2145	351	32.2	8.4	19.6	98.1	1258	266	4.6	2753
13	1.20	2222	311	33.8	8.1	20.4	95.8	1415	238	4.4	2932
14	1.19	2405	266	35.2	7.1	19.9	95.8	1345	205	4.4	3170
15	1.15	2290	285	36.0	6.4	17.4	93.0	1475	226	4.5	3271
16	1.15	1941	331	36.8	5.9	17.1	95.8	1681	264	4.3	3425
17	1.11	2379	333	36.8	5.9	17.7	93.1	1506	287	4.9	3170
18	1.10	2490	342	38.3	5.0	16.3	93.3	1655	275	4.6	3387
19	1.09	2726	349	37.4	5.4	15.7	94.2	1733	285	4.2	3501
20	1.08	2591	235	37.9	5.6	16.4	92.9	1919	196	3.8	3433

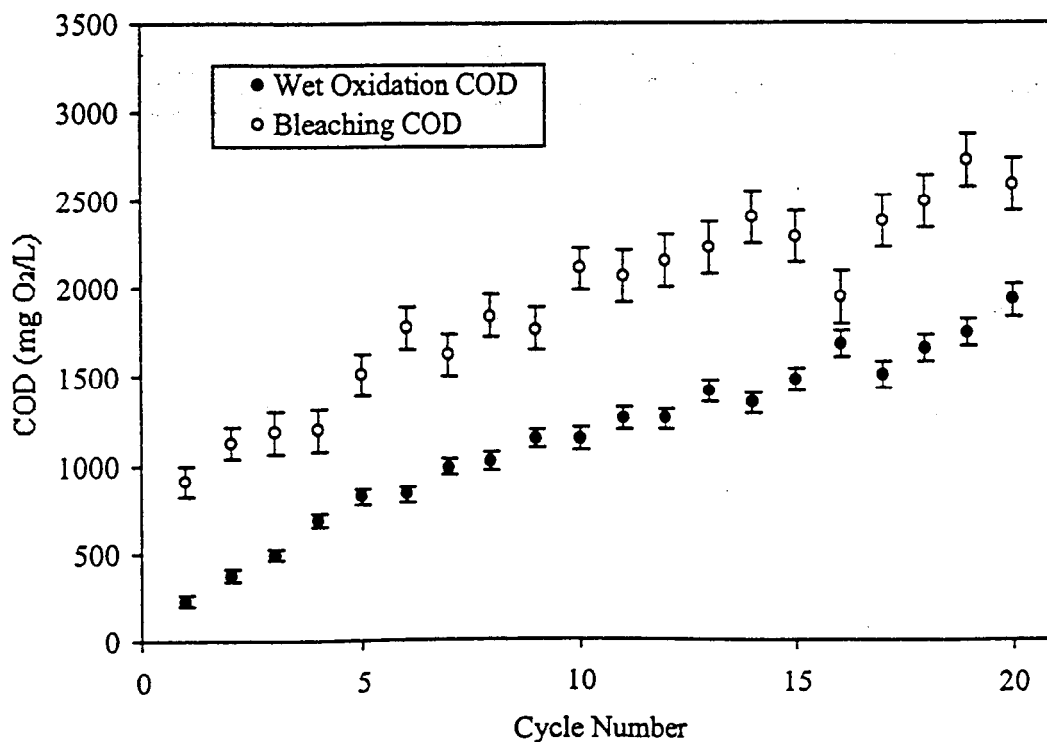


Figure 4: Chemical oxygen demand of POM liquor after bleaching and wet oxidation.

The wet oxidation COD data were modeled following the formalism developed by Li *et al.* [17]. In the general model for analysis of the kinetics of wet air oxidation (WAO), the easily-oxidized starting material (termed A) reacts along two pathways, as shown in Figure 5.

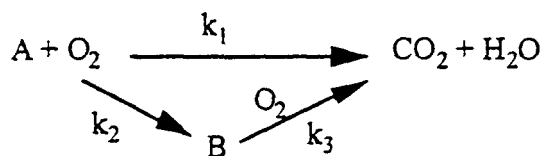


Figure 5: Reaction network for the model of Li *et al.* [17].

Along the first pathway, the starting material reacts to carbon dioxide and water. Along the other pathway, the starting material is partially oxidized to form hard-to-oxidize species (termed B). The hard-to-oxidize species eventually react to form carbon dioxide. This model was extended for use with POM wet oxidation by Birchmeier [18]. In the case of the cyclic experiment described here, the kinetic expressions derived from this model can be simplified to Equation (1), if one assumes that k_3 is slow relative to the other rates.

$$COD_{wo}(n) = [COD_{wo}(n-1) + E(COD_B(n) - COD_{wo}(n-1))] (1 - k_3 t) \quad (1)$$

In Equation (1), $COD_{wo}(n)$ is the COD after wet oxidation of the n th cycle, $COD_B(n)$ is the COD after bleaching of the n th cycle, E is a constant that is essentially the ratio of k_2/k_1 , k_3 is the rate of oxidation of the hard-to-oxidize species, and t is the duration of wet oxidation. Figure 6 compares the wet oxidation COD data with the model using least-squares estimates for the values of E and k_3 ($k_3 = 0.00058 \pm 0.00015 \text{ min}^{-1}$; $E = 0.245 \pm 0.047$). The values were obtained using the “solver” add-in of Microsoft Excel. The errors were estimated from the 95% confidence contour which was generated using a formalism that is based on the F-statistic.

The value of the constant E suggests that approximately 75% of the organic material that was removed from the pulp and dissolved in the liquor during the delignification step was rapidly converted to carbon dioxide during wet oxidation. The remaining material was converted to a hard-to-oxidize species, as is typically observed in WAO. The reaction of sodium acetate under the same wet oxidation conditions gave a rate constant of 0.00029 min^{-1} , which suggests that the hard-to-oxidize material generated during wet oxidation had a reactivity that is similar to that of acetate. Furthermore, acetate is often observed to be the rate-limiting species during WAO of organic-containing waste waters [17]. Methanol, oxalate, succinate, and malate have all been shown to react at a measurable rate when tested with other POMs under similar conditions. Thus, these experiments suggest that there is no organic species that will not be ultimately eliminated by the wet oxidation reaction in steady-state operation of the proposed process.

The model was extended to 50 cycles and displayed in Figure 6 to illustrate that the extrapolated wet oxidation COD would reach an asymptotic value of $21001 \pm 340 \text{ mg O}_2/\text{L}$. Since the reaction of the hard-to-oxidize organic material is approximately first-order, the COD level increased to the point where the amount of material lost during a wet oxidation stage is equal to the amount formed from the fresh organic material dissolved during delignification. Although the experiment was not continued to 50 cycles, the final COD value was 90% of the estimated limiting value. Even with this loading of organic material, the effectiveness of POM delignification was not diminished.

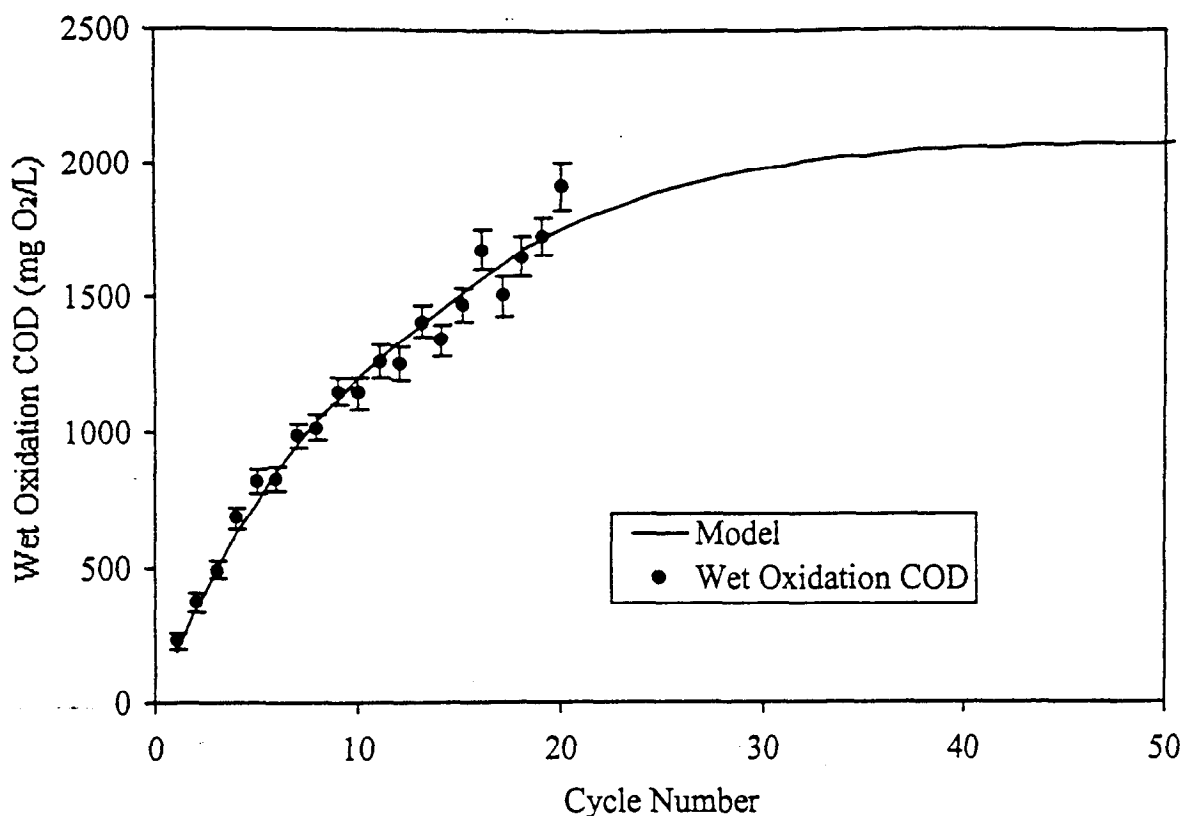


Figure 6: Comparison of predictions of WAO model to wet oxidation COD values.

Calculation of the carbon balance data suggests that all of the organic material removed from the pulp during delignification is either being lost as CO₂ or accumulated in the liquor. Figure 7 shows CO₂ production for the 20 cycles. The error bars associated with the data points are associated only with the CO₂ test and do not attempt to indicate repeatability of the bleaching and wet oxidation. The trend of the data in Figure 7 to higher CO₂ production was likely due to both the increased reaction of hard-to-oxidized species as their concentration increased and the increased delignification efficiency of the latter cycles.

Unfortunately, the pulp yield data are not sufficiently accurate to obtain a good estimate of carbon entering the system during each delignification cycle. Thus an average value was calculated for the full 20 cycles. The central line in Figure 7 represents the theoretical CO₂ that would be collected if all the losses in pulp yield, averaged over 20 cycles, were converted to CO₂ and H₂O. This value was 3174±440 mg/L. Corrections were made for COD accumulation in the liquor. The other solid lines represent the 95% confidence interval while the dashed lines show the minimum and maximum observed for the pulp yield data set. The majority of the data set for the measured CO₂ lies within the confidence interval for the CO₂ production estimated from pulp yield. The average value of CO₂ production observed was 2891±175 mg/L. Given the 95% confidence intervals of both the expected and observed CO₂ production overlap, we conclude that all of the carbon being removed from the pulp is either being eliminated as CO₂ or accumulates in the liquor, within experimental error.

Since carbon monoxide emissions could be a potential loss of carbon from the system, which would go undetected, the CO evolution for a wet oxidation reaction similar to the one described in this set of experiments was determined to be equivalent to <0.03 kg of CO/ton of pulp processed. The CO evolution for a bleaching reaction was equivalent to 0.5 kg of CO/ton of pulp produced. Since this value corresponds to less than 20 mg CO₂/L, the amount of CO produced was assumed to be negligible for the carbon balance calculations.

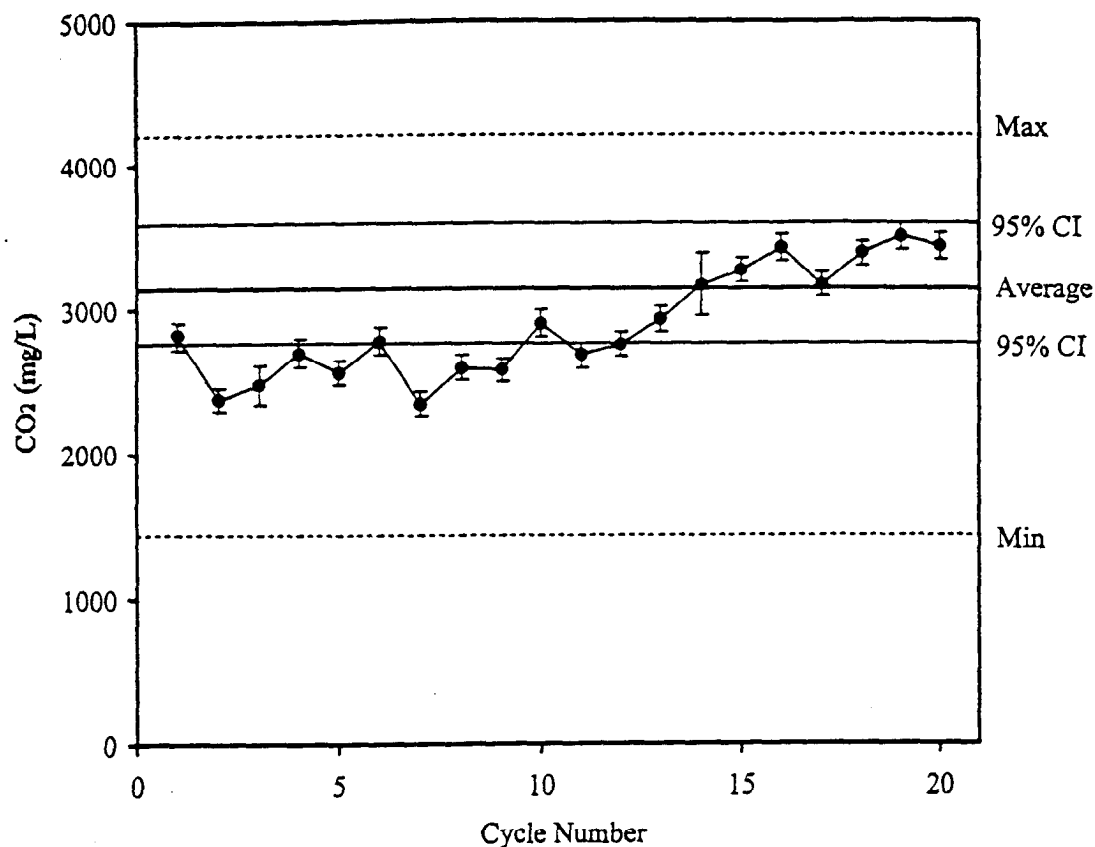


Figure 7: Total CO₂ production during delignification and wet oxidation.

CONCLUSION

By careful collection and reuse of wash waters and condensates, we have demonstrated that the POM process can eliminate sufficient organic material during wet oxidation to achieve a steady-state organic load in the liquor. From an analysis of the wet oxidation kinetic model, we conclude that if all the species formed during the reaction react at a measurable rate, then a steady-state COD value will be reached. The rate constant estimated from the data is similar to the rate constant observed for the oxidation of acetate under the same temperature and oxygen pressure. Furthermore, the COD values observed during this experiment reached 90% of the asymptotic value without affecting the delignification performance. Since we have demonstrated effective delignification, sufficient regeneration of POM liquors, and approach to a steady-state COD value in liquor, a closed-mill POM-based process is feasible.

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