

Electrochemical Delignification of Wood Pulp Using Polyoxometalate Mediators

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ABSTRACT

It has been found that polyoxometalates (POMs) can act as mediators in the electrochemical oxidation of lignin in pulps. An electrochemical cell, with a Nafion[®] membrane separating the anode and cathode compartments, was used in the delignification experiments. A softwood kraft pulp was placed in the anode compartment with a buffered 0.01M solution of the polyoxometalate $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$. During electrolysis the lignin content of the pulp was reduced from kappa number 26 to 6. The energy required for this delignification was equivalent to 120 kW-hr per ton of pulp. At \$0.05/ kW-hr, the cost for this 20-point drop in kappa number would be \$6 per ton of pulp. Based on this and other data, it may be both technically and economically feasible to delignify pulps electrochemically using POMs as mediators. The POMs are neither consumed nor modified during the reaction and can, therefore, be recovered and reused in this novel, closed-mill, delignification process.

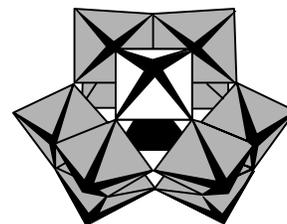
INTRODUCTION

A significant amount of work has been concentrated on using enzymes, derived from wood-rotting fungi, to remove lignin from wood. These enzymes work by using transition metals within organic ligands to shuttle electrons to oxygen resulting in the oxidation and removal of lignin from the wood while leaving the cellulose components intact. However, enzymatic technology is not generally used on an industrial scale because of their expense, slow reaction rates and susceptibility to oxidation and thermal degradation. POMs can function as inorganic analogs of these enzymes, facilitating control of complex transition-metal chemistry in water.

POMs are early-transition-metal, oxygen-anion clusters and are a large, structurally diverse and rapidly growing class of inorganic compounds. [1,2] They are formed by the condensation of common, soluble oxoanions of vanadium, molybdenum and tungsten. Additionally, a variety of redox-active transition metals can be substituted into the POM structures. POMs exhibit a number of properties that make them useful in industrial applications. They are

reversible oxidants that are water-soluble, thermally stable, oxidatively stable, minimally toxic, relatively inexpensive and easily synthesized. Additionally, POMs offer tremendous flexibility as many of their key physical properties, such as redox potential, acidity, charge, solubility, etc., can be controlled to a marked degree by choice of precursors and conditions. It is unlikely if another class of compounds exists whose properties can be so extensively and readily altered. POMs can range in size from 9 Å to over 30 Å. The most common and most thoroughly investigated structure is the Keggin anion (ca. 11 Å) shown in Figure 1.

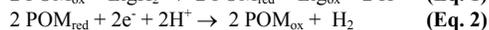
Figure 1. A substituted, α -Keggin $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$ heteropolyanion displayed in polyhedral notation. Each polyhedron represents a main-group or transition-metal atom at its center with oxygen atoms at each of its vertices. The black tetrahedron in the center represents the oxide of the Si atom, the eleven gray octahedra represent the oxides of the structural W atoms and the white octahedron represents the oxide of the substituted V atom.



These novel POM systems are currently being studied and optimized for use in a closed-mill delignification process of wood pulp fibers. Their performance, in the context of pulp bleaching, is indicated by the capacity to reduce the kappa levels of softwood kraft pulps from 30 to below 5 while retaining viscosity above 20 mPa-s. It is now clear that POM delignification technology is applicable both toward achieving a totally-chlorine-free (TCF) closed-mill process in the context of pulp bleaching and toward the cost-effective expansion of capacity of recovery-boiler-limited pulp mills. [3]

In the proposed electrochemical bleaching process, shown in Figure 2, POMs are utilized as recoverable and regenerable intermediaries in the electrochemical delignification of wood pulp. As currently envisioned, a closed bleaching mill will consist of five unit operations: electrochemical bleaching, pulp washing, concentration of wash water, removal of non-process elements (NPEs) and wet air oxidation (WAO) of dissolved organic compounds. During the bleaching step, dilute POM solutions are applied to pulp in an electrochemical cell. In this operation, the POMs are reduced while lignin is selectively oxidized and dissolved into the bleach liquor. The POMs will then be electrochemically regenerated within this same reactor. Thus, a relatively small amount of POM catalyst will be repeatedly used in multiple reduction and oxidation cycles within the same reactor. Equations 1 and 2, below, summarize these reactions. (In Equations 1 and 2, POM_{ox} and POM_{red} represent the oxidized and reduced polyoxometalates

respectively; and LigH_2 and Lig_{ox} represents the reduced and oxidized lignin.) Depending upon the configuration of the electrochemical reactor, hydrogen and sodium hydroxide may be produced. The hydrogen could be used as a fuel or chemical agent anywhere in the pulp mill while any sodium hydroxide would be returned to the POM stream to maintain the chemical balance of the POM system.



Next, the POM is separated from the bleached pulp with pressing and washing; recovery of the POMs in this step is important to the economic viability of the process. The POM liquor is then concentrated and the wash water recovered. At some point in the process, there must be a step to remove NPEs from the POM stream. These include undesirable elements from the pulp, e.g., calcium, iron, copper, etc., and chemicals carried over from the kraft pulping process. Finally, the dissolved organic compounds must be separated from the POM stream. Currently, we envision their complete mineralization to carbon dioxide and water. Under the aggressive aerobic conditions of this step, POMs initiate and catalyze the wet air oxidation (WAO) of dissolved lignin and polysaccharide fragments introduced during the bleaching step. [5] As a consequence, carbon dioxide and water are the only by-products of the POM delignification process.

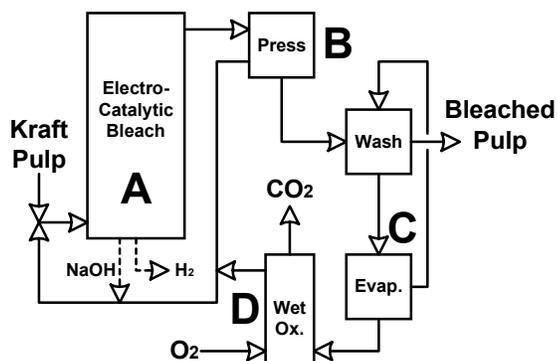


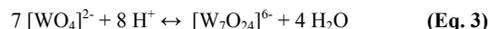
Figure 2. Simple flow diagram depicting the important unit operations of a potential electrochemical delignification process using POMs: electrochemical delignification tower (A), pulp pressing and washing (B), wash water evaporation and NPE removal (C), and the wet-air-boxidation tower (D).

EXPERIMENTAL

The various polyoxometalate (POM) salts used in experiments were synthesized according to literature procedures [4]. In some cases, the oxidized form of the POM was prepared, in others, the reduced form was prepared and had to first be oxidized in the electrochemical reactor prior to the addition of pulp and delignification reactions.

The electrochemical cell, from Electrosynthesis Company, is shown in Figure 3. The 100 mL of POM

solution in the anode compartment was 0.01 M for all the delignification reactions. In some delignification reactions, a buffer was employed to control the pH. In these cases, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to a concentration of 0.08 M. Tungstate does not buffer via protonation and deprotonation reactions, rather reversible hydrolysis and condensation reactions control the acidity of the solution [3a,5], as shown in Equation 3. A laboratory, softwood kraft pulp (0.4 g) was placed in an annular configuration inside the Pt-mesh electrode. In the cathode compartment, 50 mL of 0.05 M Na_2SO_4 was placed with Pt-wire electrode. The entire electrochemical cell was set in a heated water bath. A Protek model 3015 power supply was used to control the voltage to the cell. A voltmeter and ammeter were used to monitor the electrical power consumed by the reaction. Typically, the applied voltage was in the range of 2.5-4 V and the current was 2-6mA. Several reactions were done in some cases so that enough pulp could be combined to do TAPPI microkappa numbers and pulp viscosities.



In experiments where the efficiency of the electrochemical oxidation of POM solutions was measured, the same cell configuration was used with a few variations. The concentration of the $\text{K}_6[\text{SiVW}_{11}\text{O}_{40}]^{6-}$ and Na_2SO_4 were varied for different reactions. A buffer wasn't used in any of the reactions. All these reactions were performed at room temperature. Magnetic stirrers were placed in both halves of the cell. And small aliquots of POM solution were tested for the amount of oxidation taking place during the course of the reaction.

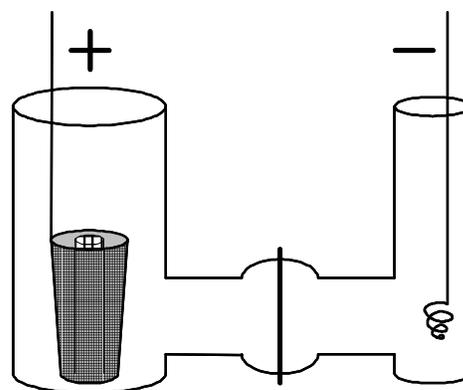


Figure 3. Electrochemical cell used in delignification experiments. POM solution was placed in the anode chamber (left), the pulp was placed in an annular configuration inside a Pt-mesh electrode (the center cylinder was made of a nylon mesh so that it contained POM solution but no pulp), a Na_2SO_4 solution was placed in the cathode cell (right) where H_2 was produced over Pt wire. The two cells were separated by a Nafion® cation exchange membrane.

RESULTS AND DISCUSSION

The results for electro-catalytic delignification with various POM intermediaries are shown in

Table 1. In previous work where POMs were applied as stoichiometric oxidants [3b], the POM anion, $[\text{SiV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{5-}$ [synthesis in ref. 4a], had proven to be an effective delignifying agent. Indeed this is the case again as this POM was able to reduce the pulp from a kappa number of 26 to 7. The power consumption for this experiment was 90 kW·hr/ton. However, at the end of the experiment, the $[\text{SiV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{5-}$ was 30% reduced, it was estimated that an equivalent of 30 kW·hr/ton would be needed to return the POM to the fully oxidized state, the state it was in at the beginning of the experiment. At \$0.05/kW·hr the electrical cost for this delignification experiment is approximately \$6 per ton. However, this delignification experiment required 32 hours to complete, significantly longer than is feasible. In most of the previous work [3c], the $[\text{SiV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{5-}$ anion was used at temperatures between 125 and 140°C, which required 1 to 3 hours (depending on POM concentration) to achieve a similar level of delignification to the data in Table 1. However, with the electrochemical cell shown in Figure 3, we were limited to a maximum temperature of 95°C and thus needed extensive reaction times to achieve a significant level of delignification. Therefore, we needed to seek POM anions that react faster with lignin.

In moving toward a more aggressive POM, $[\text{SiCo}^{\text{III}}\text{W}_{11}\text{O}_{40}]^{5-}$ was tried [synthesis in ref. 4a]. In past work [unpublished], significant reductions in pulp viscosity indicated that this POM may not be selective enough to be used for delignification of pulp; this was the case again. However, we were able to dramatically reduce the reaction time and temperature.

Table 1. Electrochemical delignification of softwood kraft pulp is summarized for various POMs used as mediators. The POM concentration was 0.01 M in all cases. The concentration of Na_2WO_4 was 0.08 M in the buffered reactions. The potential applied across the cell ranged from 2.5-4 V producing a current of 2-6 mA. A control using Na_2SO_4 in the anode compartment was also performed.

POM	Temp (C)	Kappa	Time Hr.	Visc. mPa-s	Final pH
Initial		26		67	
$[\text{SiVW}_{11}\text{O}_{40}]^{5-}$ Buffered	95	7	32	23	7.9
$[\text{SiCoW}_{11}\text{O}_{39}]^{5-}$ Buffered	66	5	8	11	5.0
$[\text{CoW}_{12}\text{O}_{40}]^{5-}$	95	5	8	16	2.2
$[\text{AlMn}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ Buffered	85	5	8	19	7.3
$[\text{SO}_4]^{2-}$	86	23	8	57	2.2

Work with $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ showed improvement [synthesis in ref. 4b]. This POM was able to delignify from kappa 26 to 5 after 8 hours at 95°C. This experiment consumed 240 kW·hr/ton (~\$12/ton), with the POM being at approximately the same oxidation state at the end of the experiment as at the

beginning. However, due to this POM anion's stability, a buffer could not be used to maintain a higher pH for the reaction.

In some preliminary work, $[\text{AlMn}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ [synthesis in ref. 4c] was used in an electro-catalytic experiment. Analytical procedures for this POM system currently limit a full assessment of this experiment; however, the delignification results show some promise. We are continuing our effort to search for a POM with the proper balance between the reaction rate at or below 95°C and delignification selectivity.

The results for experiments that assess the electrical efficiency of the POM oxidation are shown in Figure 4. These experiments were done using the reduced $[\text{SiV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ anion without a buffer. One can see that at low voltages, electrical efficiencies near 100% can be achieved. As one increases the voltage, the efficiency drops as electrical energy is wasted in the production of oxygen at the anode. However, this effect can be reduced with higher POM concentrations; a condition that would increase the delignification rate in an electro-catalytic reactor as well. The reaction current and the POM oxidation rates for various concentrations and cell potentials are shown in Table 2.

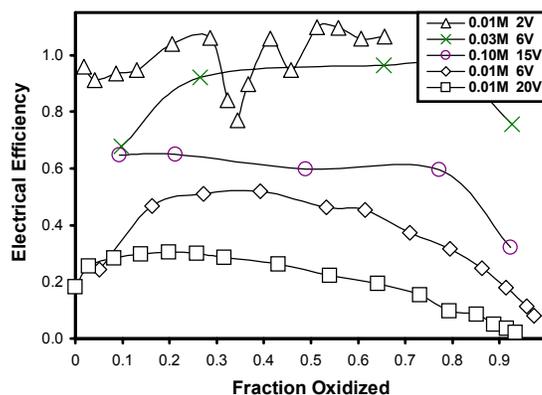


Figure 4. Electrical efficiency of POM oxidation is shown as a function of oxidized and reduced POM concentrations and the cell potential. Experiments were performed using reduced $[\text{SiV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ anion, without a buffer, in the electrochemical cell depicted in Figure 2. At lower efficiencies, significant amounts of oxygen were produced at the anode. At elevated efficiencies, the pH remained relatively constant near pH 6, but at lower efficiencies, the pH dropped below 2.

Table 2. Reaction current and the time required to oxidize 100 mL of the POM solutions for the experimental results shown in Figure 3.

POM Conc. (mol/L)	Applied Potential (V)	Current at 50% oxidation (mA)	Time for full oxidation (hr)
0.01	2	1.3	24
0.01	6	13	6
0.01	20	82	2
0.03	6	29	3
0.10	15	240	2

CONCLUSIONS

Preliminary studies indicate the potential for utilizing electrochemical methods with the polyoxometalate delignification process. Experiments indicate that electricity can be used efficiently for the oxidation of POMs. This provides an additional degree of freedom in evaluating design options for the POM process. It also opens up the potential to use POMs with oxidation states that cannot be regenerated with oxygen. This increases the likelihood of finding a POM that can be used at temperatures below 100°C or utilizing POMs with multiple oxidation states. Furthermore, one may also design a system wherein catalytic amounts of POMs can be used as mediators in the electrochemical oxidation of lignin in pulps. Initial experiments, described in this paper, show that POMs used in this manner can achieve a 20-point drop in kappa number on softwood kraft pulps with power consumption as low as 120 kW-hr/ton. At \$0.05/kW-hr, the electrical costs would be \$6/ton, an economically reasonable number. While the optimum balance between POM activity and reaction conditions is still being explored, these results show promise.

ACKNOWLEDGMENTS

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DISCLAIMER

The use of trade, firm or product names is for the convenience of the reader and is not intended to be an endorsement by USDA of any product or source to the exclusion of others which may be suitable.

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