

THERMODYNAMICALLY STABLE, SELF-BUFFERING POLYOXOMETALATE DELIGNIFICATION SYSTEMS

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ABSTRACT

Recent developments in the area of polyoxometalate (POM) chemistry have created thermodynamically stable systems that are self-buffering and multifunctional. Furthermore, they are readily synthesized from simple, commercially available precursors. These novel POM systems are currently being studied and optimized for use in a closed-mill delignification process of wood pulp fibers. Two key tasks have been the points of focus for the program. First, the selective, anaerobic delignification of softwood kraft pulps by aqueous POM solutions. Their performance, in the context of traditional 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 has also been shown that they can fully and effectively delignify kraft pulps and soda AQ pulps starting from kappa levels as high as 120. The second key process task is the regeneration of the POMs oxidative capacity using oxygen. Additionally, under these reaction conditions, the POMs aid in the wet air oxidation (WAO) of the dissolved organic byproducts from the delignification step. Therefore, POMs can be continuously recycled in a closed process in which the consumable oxidant is oxygen and the primary byproducts are carbon dioxide and water. It is now clear that POM delignification technology is applicable both toward achieving a TCF closed-mill process in the context of traditional bleaching and toward the cost-effective expansion of capacity of recovery-boiler-limited pulp mills. This report will discuss the fundamental thermodynamic, kinetic and physical chemistry of these new POM system as well as their application in close-mill delignification of wood pulp.

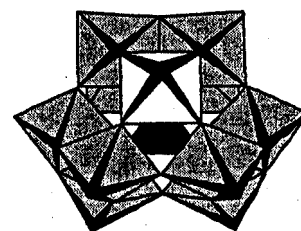
INTRODUCTION

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 feasible 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 host 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 doubtful 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 oxide of the substituted V atom.



In the proposed process, shown in Figure 2, POMs are utilized as recoverable and regenerable intermediaries in the delignification of wood pulp by oxygen. As currently envisioned, a closed bleaching mill will consist of five unit operations: anaerobic bleaching, pulp washing, concentration of wash water removal of non-process elements (NPEs) and aerobic POM regeneration concurrent with the wet oxidation of dissolved organic compounds. In the bleaching step, fully oxidized POMs are applied to pulp under oxygen-free conditions. During this operation, the POMs are reduced while lignin is selectively oxidized and dissolved into the bleach liquor. Next,

the POM is washed from the bleached pulp; extensive recovery of the POMs in this step is critical 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 pulping process. Finally, the reduced POM is regenerated, using oxygen, for the next bleaching application. Additionally, under the aggressive conditions of this step, POMs initiate and catalyze the wet air oxidation (WAO) of dissolved lignin and polysaccharide fragments introduced during the bleaching step. As a consequence, carbon dioxide and water are the only by-products of the POM delignification process.

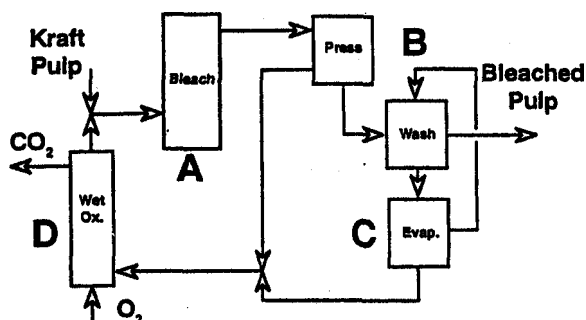


Figure 2. Simple flow diagram depicting the important unit operations of the POM delignification process: delignification tower (A), pulp pressing and washing (B), wash water evaporation and NPE removal (C), and the POM reoxidation and wet oxidation tower (D).

EXPERIMENTAL

In general, POM solutions were synthesized by heating a mixture of commercially available hydroxides or neutral or anionic oxides of transition-metal or main-group elements in water. A concise nomenclature was devised to describe these POM systems. For example, an aqueous solution referred to as $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}\text{O}_{40}]$ was synthesized by heating NaOH , Na_2SiO_3 , V_2O_5 , MoO_3 and WO_3 in molar ratios of 4.9, 1, 0.45, 1 and 10.1 respectively in water to 210°C under O_2 in a well-stirred, 316-SS Parr reactor.

For delignification reactions, aqueous POM solutions were mixed with pulp and placed in a 316-SS Parr reactor equipped with a tapered helical screw for mixing. These pulp slurries were then purged with N_2 and heated to the reaction temperature and held for a specified length of time.

For POM washing experiments, a pulp sample was taken after a 0.5 M POM delignification reaction and diluted by a factor of three and mixed to homogenize the suspension. This was then filtered into a sintered-glass Büchner funnel. An amount of

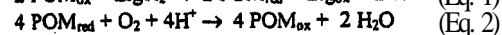
wash water corresponding to a three times dilution factor for a 10% csc. pulp was drawn through the pulp pad. This usually took 0.5 to 2 minutes. The pulps were then analyzed for metals using ICP-OES.

For POM reoxidation and WAO reactions, reduced POM solutions were placed in a 316-SS Parr reactor equipped with a gas-entrainment impeller. These solutions were then purged with N_2 and heated to the reaction temperature at which time 2.1 MPa of O_2 was introduced to initiate the reaction.

Pulp properties were determined using standard TAPPI procedures. The level of organic compounds in the POM solutions was measured using standard procedures for chemical oxygen demand. The CO_2 produced during the reactions was determined by passing head gases through and determining consumption of a $\text{Ba}(\text{OH})_2$ solution. Dissolved CO_2 was also determined. CO levels were determined by IR spectroscopy of the reaction head gases. The POMs in solution were monitored by ^{51}V , ^{27}Al and ^{183}W NMR spectroscopy and cyclic voltammetry.

RESULTS AND DISCUSSION

The POM solutions used in this work are unique systems that can be engineered to impart targeted properties. These systems are a complex, thermodynamically-controlled mixture of POM anions that is in a constant state of flux through hydrolysis and condensation reactions.[3] The distribution of these species changes to neutralize process perturbations. The most functional evidence to support this is the system's ability to maintain a relatively constant pH during the delignification and reoxidation reactions. During delignification, a hydronium ion is produced for each POM reduced (Equation. 1). Without a buffer, the pHs of the final solutions shown in Table 1 would have fallen below a pH value of 2. (This has been confirmed using POMs without a buffering component.) However, for the POM systems used here, a nearly neutral pH is maintained within a small range. (The pH actually rises somewhat due to the relative pH stability of reduced versus oxidized species.) The system then returns to its original state during its regeneration when a proton is consumed for each POM anion oxidized (Equation. 2).



The utility of POMs for the delignification of wood pulp has been studied for several years.[4-6] Delignification results for a variety of chemical softwood pulps are summarized in Table 1 while Table 2 shows a selected comparison of handsheet properties. POMs are effective over a broad range of lignin content proving their potential benefit in developing TCF bleaching sequences and sulfur-free

pulping schemes. From Table 1, the comparison of the 48% yield of a conventional kraft cook to kappa 31 with the 51 and 49% overall yields of kraft-POM and sodaAQ-POM sequences to kappas 29 and 33 respectively, exhibits the potential for POMs to increase overall pulp yields. Furthermore, since the proposed POM recovery process incorporates the WAO of dissolved organics, the use of POMs at higher kappa numbers has the potential to expand the pulping capacity of recovery-boiler-limited mills.

Table 1. Delignification of various commercial and laboratory softwood pulps using 0.5 M $\text{Na}_{5(1.9)}[\text{SiV}_{1(0.1)}\text{MoW}_{10(0.1)}\text{O}_{40}]$. POM delignification reaction conditions were generally 3% consistency, 135-145°C and 0.5-1.5 hrs. The POM solutions were generally reduced by about 30-50% and started near pH 5.5 and finished near pH 7.0. Exceptions include the K# 65 Kraft which was done at 3% csc. at 145°C for 7 hrs. and the K# 120 SodaAQ which was done at 0.4% csc. at 140°C for 6 hrs.

Pulp	Initial Pulp Properties			Final Pulp Properties		
	% Yield on wood	K#	η mPa-s	% Yield on wood	K#	η mPa-s
Kraft		31	30		4	23
Kraft		28	41		2	29
Kraft-O ₂ Delig		18	24		5	20
Kraft	48	31	35			
Kraft	53	71		51	29	40
SodaAQ	53	68		49	33	36
Kraft		65			8	26
SodaAQ	67	120		46	9	27

Table 2. Handsheet properties for a partially bleached softwood kraft pulp (kappa 31, viscosity 55 mPa-s) using a conventional DE sequence compared to POM delignification (0.5 M $\text{Na}_{5(1.9)}[\text{SiV}_{1(0.1)}\text{MoW}_{10(0.1)}\text{O}_{40}]$, 3% csc., 135°C, 15 hrs.) with an alkali extraction. (Values in parentheses are standard deviations.)

Pulp Delignification Sequence	DE	POM-E
Kappa Number	5	4
Viscosity	47	35
Yield	92	92
Directional Brightness	33.0(0.4)	37.4(0.2)
Opacity (%)	66.3(0.2)	60.6(0.7)
Scattering Coefficient (m ² /kg)	14.8(0.1)	14.1(0.4)
Canadian Standard Freeness (mL)	380	290
Density (kg/m ³)	760	800
Elongation (%)	4.6(0.2)	4.3(0.3)
Tensile Index (N-m/g)	94.2(6.1)	93.9(5.5)
TEA (J/m ²)	173(19)	184(13)
Breaking Length (km)	9.6(0.6)	9.6(0.6)
Tear Index (mN-m ² /g)	14.6(1.6)	12.0(2.0)
Burst Index (kPa-m ² /g)	8.02(0.34)	7.91(0.28)
Zero-Span Tensile Index (N-m/g)	131(10)	136(9)
Fold Endurance	2947(279)	3103(432)

The WAO of the organic compounds dissolved during the delignification step is critical to the successful operation of the process. Experiments where the same POM solution has undergone repeated delignification and regeneration reactions have been done to show the feasibility of WAO.[7]

Measurements of the organic content of the POM solutions shows a significant reduction in COD during the regeneration step. A more telling result, however, is the carbon balance depicted in Figure 3. It shows that the total CO₂ collected from the delignification and regeneration reactions is equal to the amount one would expect based upon the pulp yield. Previously reported results show that the POMs play a catalytic role in the oxidation of the organic compounds and allow the WAO to be done under milder conditions than is typically found in the industry.[8,9]

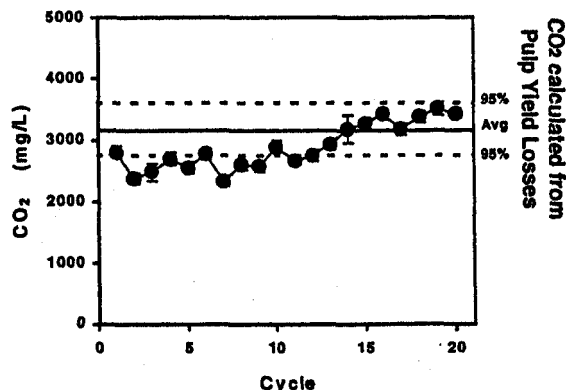


Figure 3. Plot depicting the carbon balance for a series of delignification and reoxidation reactions using the same solution of 0.5 M $\text{Na}_{5(2)}[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$. The total amount CO₂ measured for each reaction cycle is plotted against the expected amount of CO₂ based on pulp yield averaged over the twenty reaction cycles.

Table 3. Washing results for the removal of $\text{Na}_{5(1.5)}[\text{SiV}_{1(0.1)}(\text{Mn}_{0.1})\text{MoW}_{10}\text{O}_{40}]$ from delignified pulp. "Cold Wash" follows the method described in the experimental section using room temperature water. "Hot Wash" uses water near 100°C. "Sohxlet Wash" is after the pulp has been washed in a Soxhlet extractor with water for 16 hours. "Alkali Extract" refers to the pulp from cold wash after going through a standard alkali extraction and then another washing procedure. "Alkali Control" is simply another, non-alkaline, washing procedure. And "Alkali Soxhlet" is the alkali treated pulp washed for 16 hours using a Soxhlet extractor with water.

Sample	Na ppm	Si ppm	V ppm	Mn ppm	Mo ppm	W ppm
Kraft Pulp	50	14	0.2	40	2	5
Cold Wash	750	20	12	0.9	150	770
Hot Wash	625	6	6	0.3	14	135
Soxhlet Wash	20	2	0.9	2	25	30
Alkali Extract	750	4	0.8	0.6	2	17
Alkali Control	460	8	3.4	0.2	7	85
Alkali Soxhlet	25	2	0.2	0.6	1	7

One of the determining factors in the economic viability of our POM delignification process is the recovery of the POMs themselves. Since the POMs are anions that are not significantly larger than a lignin monomer and the cellulose is negatively charged, one can expect POMs to be washed easily from the pulp. The results shown in Table 3 confirm this. Indeed, with alkali, which breaks down POMs

into smaller anions like WO_4^{2-} , the pulp can be returned to nearly background levels of the POM components.

CONCLUSIONS

With continued advancements, the potential use of POMs for the delignification of wood pulp continues to satisfy the scrutiny of technological and economic viability. POMs have been used to produce pulps with physical properties equivalent to ECF technology and exceed the pulp strength of other TCF processes. Meanwhile, the POM process itself has been designed from the start as a closed system; this allows for greater flexibility when integrating it with other technologies. POMs have shown the potential to increase overall pulp yields and to increase the throughput of recovery-boiler-limited mills. The feasibilities of other unit operations in the process have also been studied and confirmed: including recovery and regeneration of the POMs as well as the WAO of dissolved organic compounds.

The development of equilibrated POM systems has addressed the questions of their long-term stability. It also provides a novel technique for buffering the reactions via the hydrolysis and condensation reactions of many POM components. Furthermore, we now have an additional degree of freedom to optimize the balance between the delignification and reoxidation reaction conditions. This allows us to develop POM formulations that uniquely fulfill the requirements of individual mill sites and placements within various locations of the fiberline.

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