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THE SECOND GENERATION OF POLYOXOMETALATE DELIGNIFICATION AGENTS FOR EFFLUENT-FREE BLEACHING

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ABSTRACT

The polyoxometalates (POMs) are a class of delignification agents that promise to provide the basis for a new closed-mill bleaching technology. Recent advances in synthesis and fundamental understanding resulted in a second generation of POMs, which are described here for the first time. They all operate at pH levels between 7 and 9, so hydrolysis of cellulose is limited and the yield levels are high. The results presented here are based on the use of $Na_6SiV_2W_{10}O_{40}$. It has been shown that this POM is effective in reducing kappa from above 30 to below 10 with limited loss in viscosity. Furthermore, it has also been applied to linerboard pulps at kappa levels of 65 and reduced the kappa to below 10, while maintaining the viscosity above 20 mPa•s. Thus, in addition to providing an alternative closed-mill technology for traditional delignification stages in bleaching, POM-based processes can also be considered a means of accepting the pulp in the bleach plant at higher kappa levels, thus reducing the load on the digesters and recovery boiler and increasing the capacity of the kraft mill

INTRODUCTION

During the past five years, a new delignification system based on the use of polyoxometalates (POMs) as reagents has been under development at the USDA Forest Service, Forest Products Laboratory (FPL), in Madison, Wisconsin. The POMs used as delignification agents are transition-metal-substituted cluster ions similar in structure to many mineral ores. These reagents are entirely chlorine free and can be used under conditions wherein they are very selective in their action on pulp fiber constituents. When applied in their active states, they can selectively oxidize lignin and related chromophores, leaving the polysaccharides undamaged. Their attractiveness as delignification agents is greatly enhanced by the fact that they can be reactivated with oxygen under conditions that can catalyze oxidation of the organic byproducts of the delignification process. Thus, they can be continuously recycled in a closed system; this. promises to provide the basis for a new class of closed-mill technologies in which the consumable oxidant is oxygen, and the primary by-products are carbon dioxide and water.

We previously reported on the first generation of POMs that were investigated in our laboratory (1-14). Here we report on a new generation of POMs that combine the most attractive characteristics of each of the first generation. Because of these advances, we are now in a position to move toward development of pilot-scale facilities for the use of POMs in delignification of commercial pulps.

BACKGROUND

Discovery of the delignifying action of POMs occurred in the context of a new program on alternative pulping and bleaching technologies specifically directed at identification of more selective oxidative systems. Selectivity was chosen as the point of focus because studies of wood-degrading fungi showed that the peroxidase enzyme systems used by fungi to degrade lignin are highly selective in their attack on aromatic constituents of the cell walls. These enzymes leave the cellulose intact so that it can later be hydrolyzed to glucose by a system of hydrolases; the fungi can then directly assimilate it as a nutrient. An interim goal of our program was then defined as duplication of the action of the peroxidase enzymes, but in systems that are useable in an industrial context

Early in the effort, we recognized that the selectivity of the peroxidases is based on the manner in which they use transition-metal ions in controlled environments to catalyze the oxidation of lignin. Indeed, there is considerable literature on organic peroxidase analogs that are effective in the oxidation of lignin in pulps. These systems, however, remain primarily of academic interest because they require complex organic platforms for the transition-metal ions, and the organic substructures are not stable at temperatures necessary to achieve high enough rates required for a feasible industrial process.

The search turned to inorganic systems that can mimic the action of the peroxidases but have the stability to be applied at elevated temperatures. The major breakthrough in our program occurred when we recognized that polyoxometalate cluster ions can provide a necessary ligand environment to mimic the function of the organic platform in many fungal enzyme systems. Thus, by placing an active metal ion in the POM structure, we simulate the action of enzymes with the level of selectivity that we were seeking.

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 phosphorous, 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 first-row transition-metal atom, such as vanadium or manganese.

In order to achieve the high degree of selectivity required, the POMs have to be applied to the pulp under anaerobic conditions. If oxygen is present, the reoxidation of the POMs can result in generation of free-radical species, which can attack and degrade cellulose. In fact, this characteristic of the POMs has become the basis for mineralizing 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, and the POMs are stable since the structural metal ions in the clusters are in their highest oxidation states. After reoxidation the POM solution can be used to bleach pulp again.

PROCESS CONCEPT

For effective use of the POMs in a delignification process that can be scaled up for commercial use, it is necessary to consider how the different phases of the chemical transformations can be organized in relation to each other. At the heart of the process, there are two complementary operations. In the first one, an aqueous solution of POM in its oxidized form is applied to the pulp under anaerobic conditions. It oxidizes the lignin in the pulp and is itself reduced. When its oxidizing capacity has declined to a point determined by overall process parameters, the spent liquor, with all the soluble organics released during the delignification operation, is separated from the pulp. In the second operation, the spent solution of POM and organics is oxidized with oxygen at an elevated temperature. Under these conditions, the reduced POM is reoxidized, and simultaneously, it catalyzes the oxidative degradation of the soluble organics to carbon dioxide and water.

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).

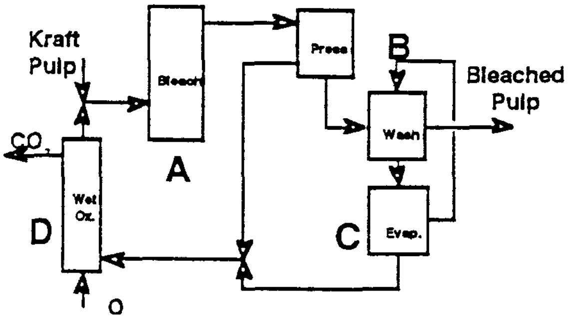

Figure 1. block diagram of the POM process.

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 also 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 and adequate recovery can be accomplished with established technologies, the focus of our program has been on improvement of 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.

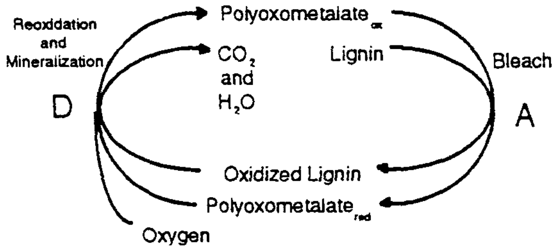

Figure 2. Net reactions of the POM process.

FIRST GENERATION POMS

Bleaching

In our first reports on POM-based delignification, we reported successful delignification in a low-consistency, multistage sequence at 125°C, using $Na_5PV2Mo_{10}O_{40}$ as the POM. The results., with respect to kappa number and viscosity, were comparable with results obtained with chlorine/chlorine dioxide based systems. The yield levels in these very early studies were in the range of 88 to 90%, how ever, due to losses attributed to hydrolysis of cellulose upon its exposure to elevated temperatures for extended periods. Work with this POM was constrained by the fact that it is not stable at pH levels above 4.

In the next cycle of delignification trials, which were carried out with $Na_5SiVW_{11}O_{40}$, we were able to reduce the duration of the individual stages and to operate successfully at temperatures below 100°C. We also demonstrated effective operation at medium consistency (11%). Two representative examples were reported. In the first, carried out at 125°C, the kappa number was reduced from 24.5 to 12.6 with a 30-minute POM stage, followed by caustic extraction. The corresponding loss in viscosity was from 28.7 to 22.2 mPa•s. In the second example, carried out at 90°C, two successive POM stages, followed by caustic extraction, reduced the kappa number from 24.5 to 11.9, with a corresponding decline in viscosity from 28.7 to 27.3 mPa•s. These two examples pointed to the possibility of further optimization of POM-based delignification.

It was with the $Na_5SiVW_{11}O_{40}$ system, as well, that the possibility of achieving very good paper properties was first demonstrated. The measured paper properties are shown in Table 1, where they are compared with properties of the same pulp after a $C/D_{30}E$ treatment.

Table 1. Paper properties of POM delignified Pulps.

	$C/D_{30}E$	POM	Control
Viscosity (mPa sec)	23.1	19.5	23.2
Burst Index (kN/g)	8.65	8.18	7.11
Tear Index (mN m^2/g)	9.03	9.30	9.45
Tensile Index (N m/g)	109.0	103.7	96.5
Zero-Span (N m/g)	160.8	148.4	150.3
Density (kg/m^3)	796.1	792.3	769.9

- 5000 rev. PFI mill (360 ml CSF)
- Initial Kappa of 24
- $C/D_{30}E$ and POM bleached to a Kappa of 4.6

In addition, data on a control sample that was subjected to the same sequence of treatments as the POM-treated pulp, but without POM, is included It is clear that the POM-treated pulp has properties that are comparable to those of the C/D_{30}E pulp.

Wet Oxidation

We previously reported that wet oxidation can be carried out effectively and POM-containing liquors can be recycled for bleaching. These wet oxidation studies, using $Na_5PV_2Mo_{10}O_{40}$, demonstrated the feasibility of achieving a low level of chemical oxygen demand (COD), together with complete reoxidation of the POM. They also demonstrated that the resulting liquors, with the residual COD, can be used for delignification and are as effective as the fresh POM solutions. Although $Na_5PV_2Mo_{10}O_{40}$ is not a feasible delignifcation agent, it remains an important POM in studies directed at characterizing the bleaching liquors and the chemical transformations that occur during wet oxidation. It is anticipated that the results of these studies will be helpful in facilitating further optimization of the wet oxidation process.

System Integration

Although the first generation of POMs did not provide the basis for a commercial process, it did allow us to explore the behavior of POMs in the context of delignification and wet oxidation. The key to successful commercialization was the identification of POMs that are effective in both delignification and wet oxidation stages. Two approaches were actively pursued in search of an integrated process. The first was the development of alternative POMs. The second was expansion of the range of operating conditions for bleaching and wet oxidation so that a wider range of POMs, including those in the first generation, might be used effectively. The current report grew from the first approach.

SECOND GENERATION POMS

We report here the development of a new generation of POMs that have a number of advantages over the first generation. In addition to being well suited to both delignification and wet oxidation, the new POMs are stable at pH levels above neutral so hydrolysis of the cellulose is significantly reduced. Another important advance associated with the introduction of this new generation of POMs has been the development of a new synthetic procedure that results in an equilibrium composition, which is inherently stable and, therefore, can be recycled repeatedly in a closed system. The new synthetic procedure is much more simple than traditional synthetic approaches. The availability of this new procedure should facilitate the design of POM production processes on an industrial scale, and it should make research in the field of POM delignification more accessible to other laboratories.

A number of new POMs, all of which appear to be stable above pH 7 and are reoxidized by oxygen, have been explored so far. These include $Na6SiV2W_{10}O_{40}$, $Na_6AlVW_{11}O_{40}$, and a group that is described by the formula $Na_5SiVW_{11-x}Mo_xO_{40}$. The one that has been studied most extensively is $Na_6SiV_2W_{10}O_{40}$, which has been routinely used to reduce kappa number from about 32 to below 10 under several different conditions, including multiple stages at 10% consistency. The yield levels, in most instances, are above 95%.

In addition to its extensive use in tests with pulps at kappa levels in the low 30s,. this POM has been used to test the feasibility of applying POM technology to higher kappa pulps. This possibility is of interest in mills that have well-established delignification and bleaching stages but could benefit from increasing the kappa level at which the pulp is removed from the digesters. The results of some trials, with a southern pine linerboard pulp at a kappa of 65, are shown in Table 2. It is clear that even if the POM stage was used to completely delignify the pulp, the viscosities are still acceptable.

Table 2. Delignification of southern pine linerboard with POMs.

POM	Final Kappa	Final Viscosity (mPa S)	Yield on Pulp (%)	Yield on Wood (%)
SiV_2W_{10}	3.6	17	87	48
SiV_2W_{10}	9.6	28	85	47

- initial kappa 65
- estimated yield 55% on OD wood
- southern pine

CONCLUSION

It is now clear that POM-based technology has the potential to outperform currently available technologies with respect to facilitating closed-mill systems and reducing environmental imp act It has also been shown that the technology is more energy efficient and quite competitive economically. The member companies participating in the consortium supporting this work are now considering the establishment of a pilot facility to demonstrate the commercial feasibility of POM-based delignification technologies.

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