Progress in the Development and Optimization of Polyoxometalate Delignification Systems

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ABSTRACT

We have reported the use of polyoxometalates (POMs) as selective, regenerable delignification agents that are inherently thermodynamically stable, and self-buffering. The re-activation with oxygen is under conditions that mineralize the organic byproducts of the delignification process. Thus, the POMs provide the basis for a closed bleach plant wherein the consumable oxidant is oxygen and the primary byproducts are carbon dioxide and water. They have been shown to reduce the kappa levels of softwood kraft pulps from 30 to below 5 while retaining viscosity above 20. Recently we have concentrated on POMs that are more efficient in the uptake of electrons from the substrate pulps per mole of POM. We have also studied the determinants of rates of electron transfer from the substrates to the POMs. All of these must be optimized in order to achieve the full economic potential of POM-based delignification. This report will summarize progress along the multiple fronts that we are investigating including the possibilities of using POMs as a complement to high yield pulping and electrochemical bleaching using POMs as mediators.

I. Introduction

The polyoxometalates (POMs) are a class of delignification agents that provide the basis for a new closed-mill bleaching technology. The POMs that are effective delignification agents are transition-metal-substituted cluster anions similar in structure to many mineral ores. They can be used under conditions that make them very selective in their action on pulp fiber constituents. In their active states and under anaerobic conditions, they can oxidize lignin and related chromophores, while leaving the polysaccharides undamaged. Upon reduction during bleaching, they can be reactivated with oxygen under conditions that catalyze oxidation of the organic byproducts of delignification and they can be continuously recycled.

We previously reported on the first and second generations of POMs that were developed for delignification in our laboratories (1-4). Here we provide an overview of that work together with more recent investigations directed at increasing the efficiency of POMs with respect to the number of electrons taken up per anion during oxidation of the substrate. We also provide a preliminary report on studies of electron transfer rates between POM anions; these rates are crucial because they may be faster than the rate of delignification thus eliminating mass transfer into the fiber as a rate limiting step.

II. Background

The delignifying action of POMs was discovered as part of a new program on alternative pulping and bleaching technologies specifically directed at higher selectivity. Selectivity was chosen for emphasis because it was known that wood-degrading fungi use highly selective peroxidase enzymes to degrade lignin. 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 early goal we set was duplication of the action of the peroxidase enzymes, but in thermally stable, inorganic systems.

We recognized that the selectivity of the peroxidases is based on the way in which they use transition-metal ions in controlled organic platforms to catalyze the oxidation of lignin. There is a considerable literature on organic peroxidase analogs, but it remains only of academic interest because they require complex organic platforms that are not stable at elevated temperatures. The search turned to inorganic systems that can mimic the action of the peroxidases but have the stability to be applied at elevated temperatures to achieve industrially viable rates. It was recognized that POM cluster anions provide a ligand environment that mimics the function of organic platforms in many fungal enzyme systems if an active metal ion is placed in the POM structure. The POMs are a class of oligomeric, metal-ion oxide clusters; the ones we have used 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 anion with a first-row transition-metal atom, such as vanadium or manganese.

In order to achieve the high degree of selectivity, 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 and polysaccharide fragments dissolved in the liquor during delignification. When the spent liquor containing reduced POM anions 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 matter is oxidized to carbon dioxide and water. The POMs are stable since the metal ions in the clusters are in their highest oxidation states.

Process Concept

For use of the POMs in a delignification process that can be scaled up for commercial use, it is necessary to consider how the different 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 and solublilizes 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 conversion of the soluble organics to carbon dioxide and water.

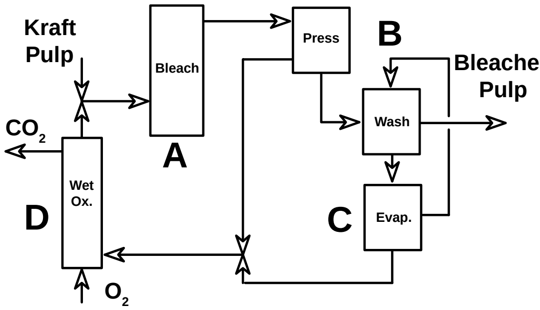

Figure 1. Block diagram of the POM process.

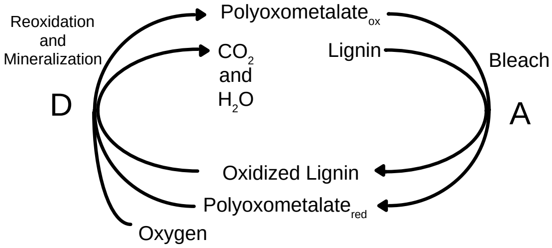

Figure 2. Net reactions of the POM process.

The process envisioned is shown in Figure 1. The key unit operations are the bleaching stage (A) and the wet oxidation stage (D). A commercial installation will also require separating the pulp from the spent liquors, washing the pulp, and concentrating the wash waters to recover the POM removed during washing. A stage for removal of non-process elements will be necessary as well. A number of preliminary studies have demonstrated that washing and adequate recovery can be accomplished with established technologies. Our program is now focused on improvement of the delignification and wet oxidation stages, and understanding the rate determining phenomena in each of the stages.

The overall chemical processes occurring in unit operations A and D are represented in Figure 2. The delignification operation (A) is represented as the reaction of the POM in its oxidized forms with the lignin to produce the soluble oxidized lignin and polysaccharide fragments, and the POM in its reduced form. The solubilized organics together with the reduced POM, are then fed into the re-oxidation stage, where the POM is re-oxidized and the solubilized organics mineralized.

Early Studies

Delignification. In our first reports we described selective delignification in a low-consistency, multistage sequence at 125^0C, using $Na_5PV_2Mo_{10}O_{40}$ as the POM. The results, with respect to kappa number and viscosity, were comparable with results obtained with chlorine/chlorine dioxide based systems. The utility of this POM was compromised 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 100^0C. We also demonstrated effective operation at medium consistency (11%). 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.

Wet Oxidation. Wet oxidation can be carried out effectively and POM-containing liquors can be recycled for delignification. These studies, using $Na_5PV_2Mo_{10}O_{40}$, demonstrated the feasibility of achieving a low level of chemical oxygen demand (COD), together with complete re-oxidation 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 from a commercial perspective, it remains an important POM in studies directed at characterizing the delignification liquors and the chemical transformations that occur during wet oxidation. The wet oxidation studies were not extended to include $Na_5SiVW_{11}O_{40}$ because its re-oxidation was too slow.

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. The approach actively pursued in search of an integrated process was the development of alternative POMs. The next generation of POMs has 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. Another important advance associated with the new group of POMs was 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. This new procedure facilitates the design of POM production processes on an industrial scale, and it will make research in the field of POM delignification more accessible to other laboratories. A number of new POMs, all of which are stable above pH 7 and are reoxidized by oxygen, were explored. These include $Na_6SiV_2W_{10}O_{40}$, $Na_6AlVW_{11}O_{40}$, and a group that is described by the formula $Na_5SiVW_{11-x}Mo_xO_{40}$. The one 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%.

Recent Progress

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 impact. It has also been shown that the technology is more energy efficient and quite competitive economically. There are, however, opportunities for further improving the economic attractiveness of the process as well as possibilities for improving the design of the process by better understanding of some of the rate controlling steps. These have been the point of focus of our effort over the past year. They will be summarizes here. They include enhancing the economics by developing more efficient POMs, They also include studies of the rate controlling phenomena that might point to alternative process designs. In addition the possibility of using POMs in the context of a sulfur free pulping has been explored. Finally some electrochemical bleaching studies have been carried out that provide deeper understanding of the processes as well as the potential of a commercial scale process if a number of process design barriers can be overcome.

Improving the economy. The approach adopted in seeking improved economy for the process has been to seek increased efficiency in the use of POMs. The current design requires the use of one POM anion in the oxidized state per electron to be abstracted from the lignin. While as noted above, we have developed POMs that are well suited for the process, the question arose concerning the possibility of enhancing the efficiency of POM utilization by designing POMs that can take up more than one electron per anion. Such POMs are theoretically possible; they are thought to be capable of uptake of two or three electrons per anion and they have been identified as multi-electron POMs. In the past year we have demonstrated that a POM with the formula $Na^+_6[AlMnW_{11}O_{40}]^{6-}$ can be oxidized to $Na^+_5[AlMnW_{11}O_{40}]^{5-}$ or reduced to $Na^+_7[AlMnW_{11}O_{40}]^{7-}$ and be isolated in stable form in each instance. Thus the POM is stable with the Mn in the Mn(II), Mn(III) and Mn(IV) forms. The oxidation potentials for both the II/III couple and the III/IV couple are such that they can be used to abstract electrons from the lignin. This system then is the basis for a 2-electron oxidant. In addition, a potential 3-electron system has been prepared; it is based on the $[SiVMn(OH_2)W_{11}O_{39}]$ anion. In this anion, two oxidation states of the V and three oxidation states of the Mn are accessible, thus allowing the abstraction of three electrons per anion from the substrate. These multi-electron systems await testing in bleaching applications, but our experience with other POMs leads us to expect that these systems will work as well as the one electron POMs. They could reduce the investment in initial charge of POM by factors of 2 or 3 respectively.

Rate controlling phenomena. In the normal course of events, it would be anticipated that the rates of delignification by POMs would depend on mass transfer phenomena in a manner that parallels the dependence for the application of other oxidants. This was found not to be the case in that the introduction of conditions that are expected to promote mass transfer does not result in corresponding increases in the rates of delignification. This led us to explore the possibility that electron self exchange may occur more rapidly than the rates of diffusion of POM anions in and out of the fiber walls. In experiments on a number of related POMs it was observed that the rates of electron exchange are indeed significantly more rapid than the rates of delignification. Thus POM_{ox}, the oxidized POM outside the fiber can oxidize the reduced POM_{red} within the fiber faster than the rates of diffusion of the anions in and out of the wall. The implications of these observations have yet to be fully assessed in preparation for design of larger reactors, but it is likely that some of the issues traditionally arising in the context of heterogeneous reactions may not arise in the case of POMs. However the variability of the rates of electron exchange with conditions may become the basis of a counter current design which is currently being assessed.

Sulfur free pulping. This is a summary of work previously reported at the 2002 pulping conference, included here to show the scope of the effort (5). Lodgepole pine chips were pulped to Kappa numbers of about 70 using soda–AQ, soda–ODiMAQ (octahydrodimethylanthraquinone), and kraft methods. At a catalyst level of 0.20% (oven-dry wood basis), cooking times for the soda cooks were significantly shorter than that for the kraft cook. The ODiMAQ catalyzed cooking time was much shorter than that of the AQ cook. It might be possible to replace the kraft process with a soda–ODiMAQ process for production of linerboard grade pulps. Delignification of the high Kappa soda–ODiMAQ pulp with oxygen and also with a polyoxometalate (POM) to Kappa numbers of about 30 resulted in higher yields of slightly weaker pulps than did pulping to Kappa 30 with the kraft process. Soda–ODiMAQ followed by oxygen sequence gave pulps much lower in viscosity than did soda–ODiMAQ followed by POM. If bleaching of oxygen-delignified pulp yields strong pulp, soda–ODiMAQ followed by oxygen delignification might be used to replace kraft pulping for the production of bleachable grade pulps. If the pulp is weak, soda–ODiMAQ followed by POM delignification might be used to replace kraft pulping.

Electrochemical delignfication using POM mediators. This is a summary of work previously reported in greater detail at the 12th International Symposium on Wood and Pulping Chemistry (6) 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 $Na_5[SiVW_{11}O_{40}]$. During electrolysis the lignin content of the pulp was reduced from kappa number 26 to 6 with limited reduction in viscosity. 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. The remaining challenge is the identification of a POM that can accomplish the delignfication at a practical rate.

FUTURE DIRECTIONS

As we look forward we anticipate that it will be possible to identify additional opportunities to enhance the efficiency of POM-based delignification from an economic perspective. We also expect to continue more detailed studies of the different alternative pathways in order to enable design of economically competitive industrial-scale systems for application of POMs in the manufacture of pulp.

Acknowledgments

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