

DELIGNIFICATION OF WOOD AND KRAFT PULP WITH POLYOXOMETALATES

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ABSTRACT

Finely divided aspen and spruce woods and a high lignin pine kraft pulp have been selectively delignified to low lignin levels using aqueous solutions of polyoxometalates under anaerobic conditions. The reduced polyoxometalates in the solutions can be reoxidized with oxygen and act as wet oxidation catalysts for the mineralization of the solubilized lignin and carbohydrate fragments to carbon dioxide and water.

INTRODUCTION

In recent years much research effort has been devoted to reducing or totally eliminating the use of chlorine and chlorine compounds in pulp bleaching. The oxygen based oxidants hydrogen peroxide, ozone and oxygen itself have been increasingly employed to totally or partially replace the use of chlorine, hypochlorite and chlorine dioxide in bleaching. Unfortunately, these oxidizing agents are not as selective in delignification as are chlorine and chlorine dioxide. The generation of free radicals in the oxygen based systems leads to more severe attack on the cellulose and hemicelluloses of the pulp than is found in delignification with chlorine or chlorine dioxide. During the past few years, a new approach to the selective delignification of pulp based on oxygen used in combination with a

class of compounds called early transition metal oxygen anion clusters, or polyoxometalates, has been studied.¹

Polyoxometalates (POMs) are a class of discrete polymeric metal-oxide anions that form spontaneously when simple oxides of vanadium (+5), molybdenum (+6), or tungsten (+6) are combined under appropriate conditions in water.² They are remarkably stable to high temperatures and oxidizing conditions and many of them are easily prepared from common, non-toxic mineral ores. In many POMs the transition metals are in the d^0 electronic configuration which dictates both a high resistance to oxidative degradation and an ability to oxidize other materials such as lignin. To date, four POMs, all of the Keggin structural class,² have been studied for their ability to delignify wood and kraft pulp.

In the delignification process envisioned, a highly selective and completely regenerable POM will be employed. In the delignification stage the completely oxidized POM complexes will be reacted with wood fibers or pulp under anaerobic conditions. During delignification, the POM complexes will be reduced and the lignin oxidized and its liberated fragments dissolved in the treatment liquor. The liquor will then be separated from the fibers and the POM complexes reoxidized using oxygen. During the reoxidation stage the conditions will be such that the POM complexes will act as wet oxidation catalysts to convert the dissolved lignin and carbohydrate fragments to carbon dioxide and water. The envisioned process will thus be a completely closed system emitting only carbon dioxide and water. Of course, some losses will occur and a small amount of POM will have to be supplied to the system. Other publications describe the process in greater detail.^{1,3-4}

In the present work finely divided aspen and spruce woods and high lignin kraft pulp were delignified using POMs.

DELIGNIFICATION OF MILLED WOOD

Wiley milled quaking aspen (*Populus tremuloides*) and white spruce (*Picea glauca*) woods that passed a No.40 mesh screen were delignified with an aqueous solution of the POM $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$. The objective of this work was to determine whether it was possible for POMs to delignify wood. To avoid the problems associated with penetration of the POM into the wood structure, very finely divided wood was used. A multi-step synthesis was used to produce the pure POM. Phosphate, acetate and tungstate buffers were added to the several POM solutions used to keep the pH of the solutions as high as possible. Without the buffers the pH would sink to very low levels and the cellulose and hemicelluloses would be severely attacked.

Table 1 shows the reaction conditions used and the results obtained on delignification of the milled aspen wood with the 0.15 molar POM solutions. The wood could be readily delignified under relatively mild conditions. For Run 3, using the potassium salt of the POM, the lignin content of the residue was reduced from 20% to 2.2% with a residue yield of 59%. If the wood had been kraft pulped to this lignin level a maximum yield of 56% would be expected. The POM delignification was thus significantly more selective than kraft pulping. Comparing Runs 3 and 32 it is seen that use of an acetate buffer resulted in considerably lower pH's during the reaction and a much slower rate of delignification. Since the residue lignin value for Run 32 was over 4% the viscosity value shown may not be accurate. Comparing Runs 3 and 36 it is seen that using the sodium salts of the POM and the buffer resulted in somewhat lower pH during the reaction and a significantly reduced rate of delignification. The residue viscosity was also somewhat reduced. As shown by the results of Run 40, going to a tungstate buffer resulted in higher reaction pH values and a somewhat increased viscosity. Using the potassium salts of the POM and the tungstate buffer might give even better results, however, this may not be possible due to the limited solubility of the potassium salts.

Table 2 shows the reaction conditions used and the results obtained on delignification of the milled spruce wood with the 0.30 molar POM solutions. Since the spruce wood contained more lignin a higher concentration of POM and a higher reaction temperature were employed. As with aspen, the wood was readily delignified using relatively mild conditions. In Run 37 a yield of 53% was obtained at 4.1% lignin in the residue. For kraft pulping to this lignin content a maximum yield of 50% might be expected. As with aspen, the POM delignification was significantly more selective. Comparing Runs 37 and 41, again we see that the tungstate buffer increased the reaction rate and resulted in a somewhat higher residue viscosity.

An attempt was made to delignify aspen pin chips (2x2x15mm) using a 0.40M solution of the POM at 125 ml per gram of wood and 125°C for 48 hours. The chips were thoroughly vacuum impregnated prior to heatup. On examination of the chips after reaction it was found that only the surface fibers had been delignified. Under these conditions, it was not possible to diffuse sufficient POM into the interior of the chips to substantially delignify them. Based on this experiment, it appears to be very unlikely that it will be possible to delignify even very thin chips or wafers with POMs. As a consequence of this, it was decided to investigate the POM delignification of high lignin pulps.

DELIGNIFICATION OF SOUTHERN PINE KRAFT LINERBOARD PULP

A quantity of southern pine kraft linerboard pulp with a Kappa number of 65 (9.7% lignin) was obtained from a pulp mill in Arkansas. Using the data of Parsad et al.,⁵ its yield was estimated to be 55%. Initially the pulp was delignified with the POM $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$ using a tungstate buffer. The reaction conditions employed and the results obtained are given in Table 3. The pulp was easily delignified to Kappa number three while suffering little cellulose degradation (retaining a viscosity of 30 mPs.s).

During the course of the present work, two new POMs have been synthesized using a new, simple, one step procedure which results in an equilibrium composition that is self buffering and inherently thermodynamically stable.⁶ As with the buffered POM synthesized by the multi-step procedure, these new self buffering POMs can be recycled repeatedly in a closed system and have been found to be much more easily reoxidized than $\text{Na}_6[\text{SiVW}_{11}\text{O}_{40}]$ (the reduced form of $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$). Due to these advantages, further work on the delignification of the linerboard pulp was performed with these POMs. The first of them to be studied was $\text{Na}_6[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$. Table 3 shows the conditions used and the results obtained in the initial experiment using this POM. Compared with the tungstate buffered $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$, a higher temperature and longer time was required to delignify the pulp to Kappa number 3. The pulp viscosity obtained was somewhat lower but still in at an acceptable value. These results can be explained by the fact that the redox potential for the new POM is considerably lower than that for $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$. This, however, allows it to be much more readily reoxidized and based on overall system considerations it is, at the present time, a very promising candidate for further study.

Two experiments were carried out with the self buffering POM to determine its performance under more practical reaction conditions. The results from these experiments are given in Table 4. Comparing Runs 61 and 63 it is seen that increasing the POM concentration while reducing the solution to pulp ratio results in a significant yield increase and also a significant viscosity decrease. At Kappa number 3, the 16 mPa.s viscosity is still high enough to indicate little loss of pulp strength. Increasing the solution to pulp ratio and decreasing the temperature as in Run 57 results in a decrease in yield but a very significant increase in viscosity. Results are thus very dependent on reaction conditions.

The most recently synthesized self-buffering POM is $\text{Na}_6[\text{AlVW}_{11}\text{O}_{40}]$.⁶ This has a redox potential that lies between those of the other two POMs used in this work. Table 5 shows the reaction

conditions used and the results obtained from one experiment on delignifying the linerboard pulp with this POM. Self buffering $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$ was also synthesized and used to delignify the pulp and the results are shown in Table 5. These results are compared under very similar conditions with those from self buffering $\text{Na}_6[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$ and the tungstate buffered pure multi-step synthesized $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$. Comparing Runs 57 and 62 it is seen that $\text{Na}_6[\text{AlVW}_{11}\text{O}_{40}]$ delignifies somewhat faster than $\text{Na}_6[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$, however, it may be somewhat less selective since both yield and viscosity are significantly lower. If the $\text{Na}_6[\text{SiV}_2\text{W}_{10}\text{O}_{40}]$ data at Kappa Number 5 were extrapolated to Kappa number 3 the yield and viscosity would probably still be somewhat higher than those of the $\text{Na}_6[\text{AlVW}_{11}\text{O}_{40}]$. More work is needed to verify this. Comparing Runs 48 and 69, it can be seen that the tungstate buffered $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$ gives a lower yield but a higher viscosity than the self buffered at the same Kappa number. The reaction conditions were, however, substantially different. The two newly synthesized POMs are of the most interest since they are more easily reoxidized than is $\text{Na}_5[\text{SiVW}_{11}\text{O}_{40}]$. Work continues on the development of new, more optimum POMs.⁶

CONCLUSIONS

Milled aspen and spruce woods and high lignin pine kraft pulp can be selectively delignified to low lignin contents with aqueous solutions of polyoxometalates. Recently developed self buffering polyoxometalates can readily delignify the high lignin kraft pulp and can be easily reoxidized with oxygen. They also effectively catalyze the wet oxidation of the solubilized lignin and carbohydrate fragments so that a closed cycle delignification system is feasible.

EXPERIMENTAL

All reactions were performed in a one liter Parr reactor. The contents were stirred using a turbine impeller at 140 RPM. Nitrogen was bubbled through the solution in the reactor for 15 minutes prior

to sealing the reactor and heatup. Reaction time was counted from the time the reactor contents reached the reaction temperature until the reactor was placed in cold water. Heat up time from room temperature to reaction temperature was about 40 minutes. After cooling the reactor contents were filtered using a weighed crucible with a fritted glass bottom (coarse). and the residues thoroughly washed with reverse osmosis water. The residue in the crucible was then air dried and finally dried at 60°C in a vacuum oven for 16 hours. The residue and crucible were then weighed and the yield calculated. Microkappa numbers were determined using TAPPI um-246; viscosities were determined using TAPPI T230 om-89. Lignin contents were determined using the 72% sulfuric acid method employed at the USDA Forest Service, Forest Products Laboratory,⁸ which is essentially the Klason lignin procedure. Reduction of the POMs was determined by titration with Ce^{IV} in 0.05 M H₂SO₄. Preparation and characterization of the POMs was carried out as described elsewhere.^{3,6-7}

LITERATURE CITED

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TABLE 1
 POM (SiVW₁₁ O₄₀)⁵⁻ Delignification of Aspen Wood (20% Lignin)

| Run | 3 | 32 | 36 | 40 |
|--------------------------------------|-------|--------|------|------|
| Conditions: | | | | |
| POM, M | 0.15 | 0.15 | 0.15 | 0.15 |
| Cation | K | Na | Na | Na |
| CH ₃ COOH, M | | 0.08 | | |
| CH ₃ COONa, M | | 0.32 | | |
| NaH ₂ PO ₄ , M | 0.2* | | 0.2 | |
| Na ₂ HPO ₄ , M | 0.2* | | 0.2 | |
| Na ₂ WO ₄ , M | | | | 0.15 |
| H ₂ SO ₄ | | | | 0.02 |
| Wood Wt., g | 1.00 | 1.00 | 1.00 | 1.00 |
| Solution, ml. | 500 | 500 | 500 | 500 |
| Reaction Temp., C | 135 | 135 | 135 | 135 |
| Reaction Time, hr. | 7.2 | 7.0 | 7.2 | 7.2 |
| Initial pH | 6.7 | 5.1 | 6.2 | 7.5 |
| Final pH | 5.6 | 4.8 | 5.3 | 6.8 |
| Results: | | | | |
| Residue Yield, % | 59 | 57 | 59 | 59 |
| Residue Lignin, % | 2.2 | 5.4 | 3.7 | 2.6 |
| Lignin Removed, % | 93 | 85 | 89 | 92 |
| POM Reduced, % | 36 | 33 | 34 | 30 |
| Viscosity, mPa.s | 33 | 28? | 31 | 36 |
| Residue Color | Cream | Lt.Br. | Tan | Tan |
| Efficiency, | 6.8 | 6.8 | 7.0 | 8.1 |
| g.lig. rem./mole POM red. | | | | |

* Potassium salt used here, sodium salts used in all other cases.

TABLE 2
 POM (Na₅SiVW₁₁ O₄₀) Delignification of Spruce Wood (29% Lignin)

| | | |
|--|------|------|
| Run | 37 | 41 |
| Conditions: | | |
| POM, M | 0.30 | 0.30 |
| Cation | Na | Na |
| CH ₃ COOH, M | | |
| CH ₃ COONa, M | | |
| NaH ₂ PO ₄ , M | 0.08 | |
| Na ₂ HPO ₄ , M | 0.40 | |
| Na ₂ WO ₄ , M | | 0.30 |
| H ₂ SO ₄ | | 0.04 |
| Wood Wt., g | 1.00 | 1.00 |
| Solution, ml. | 500 | 500 |
| Reaction Temp., C | 145 | 145 |
| Reaction Time, hr. | 4.0 | 4.0 |
| Initial pH | 6.4 | 7.7 |
| Final pH | 4.9 | 6.1 |
| Results: | | |
| Residue Yield, % | 53 | 52* |
| Residue Lignin, % | 4.1 | 3.0 |
| Lignin Removed, % | 93 | 95 |
| POM Reduced, % | 26 | 24 |
| Viscosity, mPa.s | 23 | 25 |
| Residue Color | Tan | Tan |
| Efficiency, | 7.1 | 7.7 |
| g.lig. rem./mole POM red. | | |
| * much white precipitate which dissolved in the 1% NaOH extraction liquid. | | |

TABLE 3
 POM Delignification of So. Pine Linerboard Pulp
 (9.7% Lignin = Kappa No. 65, Est. Yield = 55%)

| Run | 48 | 61 |
|--|---|--|
| POM Used | Na ₅ [SiVW ₁₁ O ₄₀] | Na ₆ [SiV ₂ W ₁₀ O ₄₀] Self Buffered |
| Conditions: | | |
| POM, M | 0.15 | 0.15 |
| Na ₂ WO ₄ , M | 0.15 | |
| H ₂ SO ₄ , M | 0.019 | |
| Pulp wt., g | 1.0 | 1.0 |
| Solution, ml. | 500 | 500 |
| Reaction Temp., C | 135 | 150 |
| Reaction Time, hr. | 6.0 | 7.0 |
| Initial pH | 7.4 | 7.3 |
| Final pH | 7.0 | 8.4 |
| Results: | | |
| Residue Yield, % | 83 (46)* | 83(46)* |
| Kappa Number | 3 | 3 |
| Lignin Removed, % | 97 | 97 |
| POM Reduced, % | 15 | 11 |
| Viscosity, mPa.s | 30 | 24 |
| Residue Color | Cream | Cream |
| Efficiency, g.lig. rem./mole POM red. | 8.2 | 10.2 |
| I Overall yield | | |

TABLE 4
 POM ($\text{Na}_6\text{SiV}_2\text{W}_{10}\text{O}_{40}$) Delignification of So. Pine Linerboard Pulp
 (9.7% Lignin = Kappa No. 65, Est. Yield = 55%)

| Run | 61 | 57 | 63 |
|--|---------|---------|----------|
| Conditions: | | | |
| POM, M | 0.15 | 0.50 | 0.50 |
| Pulp wt., g | 1.0 | 1.0 | 1.0 |
| Solution, ml. | 500 | 250 | 125 |
| Reaction Temp. C | 150 | 140 | 150 |
| Reaction Time, hr. | 7.0 | 7.0 | 7.0 |
| Initial pH | 7.3 | 7.9 | 8.5 |
| Final pH | 8.4 | 8.7 | 8.9 |
| Results: | | | |
| Residue Yield, % | 83(46)* | 85(47)* | 88(48)*. |
| Kappa Number | 3 | 5 | 3 |
| Lignin Removed, % | 96 | 93 | 95 |
| POM Reduced, % | 11 | 10 | 24 |
| Viscosity, mPa.s | 24 | 28 | 16 |
| Residue Color | Cream | Cream | Cream |
| Efficiency, g.lig. rem./mole POM red. | 10.2 | 7.0 | 6.3 |
| * Overall yield | | | |

TABLE 5
 POM Delignification of So. Pine Linerboard Pulp
 (9.7% Lignin = Kappa No. 65, Est. Yield = 55%)

| POM | Na ₅ SiVW ₁₁ O ₄₀ | Na ₅ SiVW ₁₁ O ₄₀ Self Buffering | Na ₆ SiV ₂ W ₁₀ O ₄₀ Self Buffering | Na ₆ AlVW ₁₁ O ₄₀ Self Buffering |
|--|--|--|--|--|
| Run | 48 | 69 | 57 | 62 |
| Conditions: | | | | |
| POM, M | 0.15 | 0.50 | 0.50 | 0.50 |
| Na ₂ WO ₄ , M | 0.15 | | | |
| H ₂ SO ₄ , M | 0.019 | | | |
| Pulp wt., g | 1.00 | 1.00 | 1.00 | 1.00 |
| Solution, ml. | 500 | 250 | 250 | 250 |
| Reaction Temp., C | 135 | 140 | 140 | 140 |
| Reaction Time, hr. | 6.0 | 3.0 | 7.0 | 7.0 |
| Initial pH | 7.4 | 6.1 | 7.9 | 7.6 |
| Final pH | 7.0 | 7.2 | 8.7 | 8.3 |
| Results: | | | | |
| Residue Yield, % | 83(46)* | 89(49)* | 85(47)* | 80(44)* |
| Kappa Number | 3 | 3 | 5 | 3 |
| Lignin Removed, % | 97 | 95 | 93 | 97 |
| POM Reduced, % | 15 | 16 | 10 | 9 |
| Viscosity, mPa.s | 30 | 23 | 28 | 21 |
| Residue Color | Cream | Cream | Cream | White |
| Efficiency, g.lig. rem./mole POM red. | 8.2 | 4.6 | 7.0 | 8.3 |
| * Overall Yield | | | | |

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