# CONCOMITANT USAGE OF TRANSITION METAL POLYANIONS AS CATALYSTS IN OXYGEN DELIGNIFICATION: LABORATORY BLEACHING TRIALS

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## ABSTRACT

Two different α-Keggin type polyoxometalates (POMs) in conjunction with a commercial silicomolybdate (SiMo) preparation were tested in a catalytic oxygen bleaching concept. The idea of this biomimetic concept is to harness the radical species produced in reactions of $O_2$ to effective delignification through formation of activated hydrogen peroxide *in situ*. Results of the laboratory bleaching trials showed modest delignification ($\Delta\kappa \leq 6$ units). The intrinsic viscosity of the pulp stayed high with the POM $K_6[AlMn(H_2O)W_{11}O_{39}]$ while the POM $(NH_4)_5H_4[PV_6Mo_6O_{40}]$ showed inferior selectivity (viscosity losses ≤ 95 and ≤ 228 mL/g, respectively). It is concluded that the probable reason for the rather poor delignification results is the low reoxidation rate of the tested POMs: The functionality of the catalytic bleaching concept presented should be tested further with catalysts possessing faster regeneration rates.

### Keywords

Catalytic oxygen delignification, bleaching, chemical pulp, polyoxometalate, silicomolybdate, activated peroxide

## INTRODUCTION

Since the discovery of the environmental problems inherent to the usage of elemental chlorine ($Cl_2$) in chemical pulp bleaching (*1-3*), the wood pulping industry has been looking for alternative, economically and ecologically sound, bleaching methods. This has led to emergence of elemental chlorine free (ECF) bleaching where chlorine dioxide ($ClO_2$) instead of $Cl_2$ is used. Also, utilisation of oxygen delignification as well as other totally chlorine free (TCF) bleaching techniques has increased.

Essentially, the chemistry of TCF bleaching methods is oxygen-based: in addition to oxygen gas ($O_2$), different combinations of e.g. hydrogen peroxide ($H_2O_2$), ozone ($O_3$), and peracid (e.g. $H_3CCOOOH$) treatments are used. The selectivity of oxygen-based chemicals is generally considered lower than that of $ClO_2$. For example, $O_2$ is poorly

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selective at high degrees of delignification. Therefore, if used extensively, contemporary $O_2$ bleaching techniques may lead to reduction in pulp quality and yield. Nevertheless, it has to be noted that there are problems with the ECF technology, as well: $ClO_2$ is expensive (*4*) and corrosive (*5*). Moreover, reactions of $ClO_2$ in bleaching do produce chlorinated organic compounds, albeit minor in amount and degree of chlorination—hence less persistent and toxic—compared to the corresponding compounds formed in $Cl_2$ bleaching (*6-8*).

Through improving the efficiency and selectivity of TCF bleaching methods, usage of $ClO_2$ could be decreased. During the past two decades, this subject has been widely studied (*9*). One alternative for improving the performance of oxygen chemicals is application of catalysts. In this paper, function of transition metal polyanions as oxidation catalysts is looked into in greater detail.

α-Keggin type polyoxometalates (POMs), spherical anionic metal-oxide complexes (*10*), were originally proposed as activating agents for oxygen delignification roughly a decade ago and have been vividly investigated since (*11-30*). The starting point in POM bleaching research was originally to produce a biomimetic way of lignin decomposition. The activity of POMs is based on the idea that they react selectively with phenolic lignin structures in cellulosic fibre and that they can often be regenerated with oxygen gas. Moreover, POMs are remarkably stable at wide pH and temperature ranges. Although POMs have been widely investigated, they have not been applied in the wood pulping industry. This is most probably due to inefficiency and/or complexity of the processes presented.

In this paper, a novel approach towards biomimetic lignin degradation is presented. It is known from literature (*31*) that lignin biodegradation requires, not only oxygen gas, but also hydrogen peroxide ($H_2O_2$). In connection with this, certain transition metal compounds, such as molybdates (*32-34*), have been discovered to activate hydrogen peroxide as a delignification agent. In acidic (pH ~2 – 6) peroxide bleaching using silicomolybdate (SiMo), $H_2O_2$ is activated by polyanions[§] through peroxymolybdate production. SiMo bleaching was tested in industrial scale as early as 1994 (*34*) and is reported to be utilised in the pulping industry (*35*). According to previous papers (*36,37*), SiMo-activated peroxide attacks, in addition to residual lignin structures, also the hexenuronic acid (HexA) groups present in the unbleached cellulosic fibre.

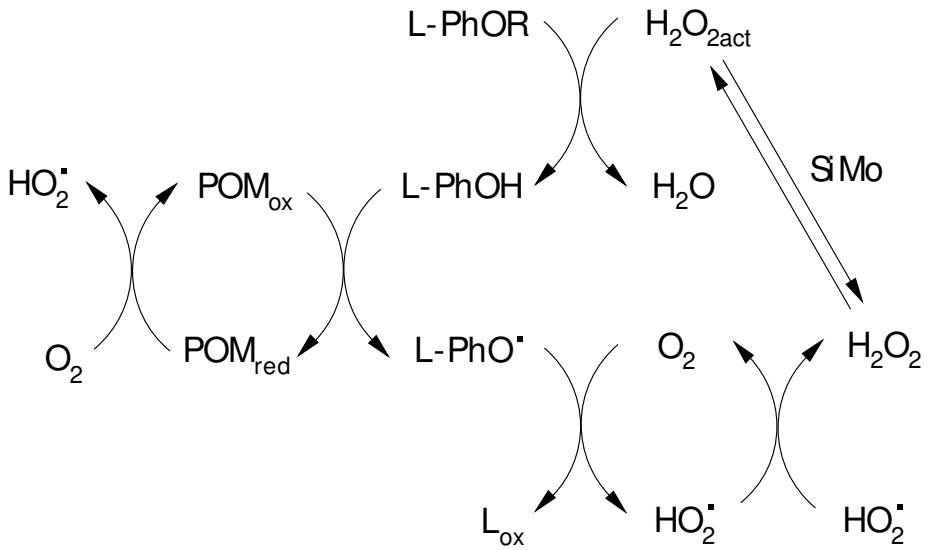
Obviously, in order to be able to catalyse delignification, SiMo requires hydrogen peroxide. Therefore, normally to SiMo-activated bleaching, $H_2O_2$ is added. An interesting and a widely acknowledged fact is, however, that in oxygen delignification and in regeneration of POM, $H_2O_2$ is formed through radical reactions (*38-40*). Kontturi *et al.* (*41*) have attempted to quantify the *in situ* peroxide production during alkaline oxygen bleaching. They reported values as high as 25 mmol/L, corresponding to 9.0 g or 0.9% $H_2O_2$ in a kg o.d. pulp, which is close to normal $H_2O_2$ dosage in SiMo-activated bleaching where 1 – 1.5% hydrogen peroxide is used (*36,42*). Hence, theoretically, it may

§ These polyanions contain molybdenum and silicon atoms in varying combinations. In fact, some of the polyanions probably are α-Keggin structures (*34*); however, in this work a commercial SiMo preparation was used, the exact composition of which was unknown. Therefore in the text the abbreviation SiMo is used for all of the possible polyanions (including α-Keggin POMs) formed due to the use of the commercial preparation—the abbreviation POM is restrained to compounds that were known for certainty to exist as α-Keggin structures in the conditions used.

be possible to combine the POM catalysed oxygen delignification and SiMo-activated peroxide bleaching into one single bleaching stage.

The aim in the catalytic bleaching concept studied in this paper is to mimic the biodegradation of lignin and to harness the radical species formed during the oxidation reactions for effective delignification. The reactions that are postulated taking place during POM/SiMo bleaching of chemical pulp are outlined in Scheme 1. The scheme shows (in the middle) oxidised POM anion ($POM_{ox}$) reacting with a phenolic lignin structure (L-PhOH)—the reaction products are phenoxy radical (L-PhO$^{\bullet}$) and a reduced POM anion ($POM_{red}$). The phenoxy radical reacts further with $O_2$ leading to an oxidised lignin structure ($L_{ox}$) and hydroperoxy radical ($HO_2^{\bullet}$); $HO_2^{\bullet}$ is also formed in oxidation of $POM_{red}$, which results in formation of $POM_{ox}$ (on the left). Dismutation (i.e. combination) reaction of the radical species produced in the reactions of $O_2$ leads to formation of hydrogen peroxide. $H_2O_2$ is activated by silicomolybdate (SiMo) and the activated peroxide ($H_2O_{2act}$) reacts further with a non-phenolic lignin structure (L-PhOR) in a reaction where a phenolic lignin moiety and water are produced. In other words, Scheme 1 suggests different reaction pathways for the phenolic and non-phenolic lignin structures. Presumably, in biological processes also, chemistry of lignin degradation is dependent on the structural characteristics of the specific lignin moieties (*43*).

*Scheme 1. The theoretical principle of POM/ SiMo bleaching. For further details, see text.*




In the laboratory bleaching trials reported in this paper, two POM catalysts ($K_6[AlMn(H_2O)W_{11}O_{39}]$ and $(NH_4)_5H_4[PV_6Mo_6O_{40}]$), a commercial SiMo catalyst, and $H_2O_2$ were utilised in different combinations to achieve delignification. The results of the experiments are used to assess the validity of Scheme 1: To what extent do the postulated chemical reactions take place during the laboratory bleaching trials? Also, the functionality and commercial potential of the POM/SiMo catalysed oxygen bleaching concept is critically discussed. Finally, conclusions and proposals for future research are made.

# EXPERIMENTAL

## Materials

Unbleached, never-dried softwood kraft pulp obtained from a Finnish pulp mill was used. The pulp was washed thoroughly with de-ionised water before the bleaching trials. $K_6[AlMn(H_2O)W_{11}O_{39}]$ (POM1) was synthesised (*44*) in Forest Products Laboratory, USDA (Madison, Wisconsin, USA) and $(NH_4)_5H_4[PV_6Mo_6O_{40}]$ (POM2) was synthesised (*45*) at Jialex laboratories in Cluj Napoca, Romania. The POMs were stored as solid salts and dissolved in distilled water before use ([POM] = 0.009 or 0.027 mol/L). The SiMo preparation (FennoAct®) used was obtained from Kemira Oyj (Vaasa, Finland). Hydrogen peroxide ($H_2O_2$) was used as a 3 w-% solution freshly prepared from a commercial 30 w-% $H_2O_2$ solution (supplied by Mallinckrodt Baker B.V., Deventer, Netherlands). The sodium acetate (anhydrous) was supplied by Fluka Chemie GmbH (Buchs, Switzerland).

## Methods

The bleaching experiments were carried out in a medium consistency (MC) mixer of our laboratory. The equipment is supplied with a powerful motor that enables mixing of MC pulp with up to 3,000 rounds per minute (rpm). The reactor vessel of the equipment is Teflon-coated.

100 g of pulp (oven dry weight) at 10% consistency was used in each bleaching experiment. Bleaching was carried out at pH 4.9 ± 0.2 and ionic strength 0.1 mol/L (adjusted with 0.5 mol/L $H_2SO_4$ and 1.0 mol/L sodium acetate) for 90 minutes at 90 ± 3 °C and 0.50 ± 0.02 MPa $O_2$ pressure (temperature and $O_2$ pressure increased slightly during the bleaching trials). Catalyst and peroxide solutions (when used) were added to the heated pulp suspension before closing and pressurising the reactor vessel. POM concentration in the bleaching trials containing catalysts was ~0.3 mmol/L or ~1.5 mmol/L (~10 or ~50 g/kg o.d. pulp) and SiMo content was 0.6 mmol/L (~0.5 g/kg o.d. pulp) calculated as molybdenum; $H_2O_2$ additions were either 0.2% or 0.5% of o.d. pulp. After pressurising the reaction vessel with $O_2$, the pulp suspension was mixed first for few seconds at full speed (3,000 rpm) to ensure even distribution of oxygen and the catalysts in the suspension. During the bleaching experiments, mixing at 45 second periods (350 rpm) every 20 minutes was used.

After bleaching, the pH of the pulps was determined and then the pulps were filtered and washed thoroughly. Kappa numbers, intrinsic viscosities, and hexenuronic acid (HexA) contents of the pulps were determined with the well-established methods (Scandinavian standards SCAN-C 1:00 & SCAN-CM 15:99 and the technique described by Vuorinen *et al.* (*46*), respectively). The bleached pulps were also alkali-extracted (10% consistency, 1 mol/L NaOH addition until pH 10-11, 60 min. treatment at 75 °C followed by filtration and washing), after which the pulp properties mentioned were determined again.

## RESULTS AND DISCUSSION

Results of the bleaching trials are presented in Table 1; during the bleaching experiments, the pH of the pulp suspension stayed virtually unchanged. The kappa number, intrinsic viscosity, and HexA content of the original, unbleached pulp were 30.0, 1188 mL/g, and 27.7 meq/kg o.d. pulp, respectively. These values are typical for unbleached softwood kraft pulp.

*Table 1*
*Pulp properties after catalytic oxygen bleaching and subsequent alkali extraction*[a]

| Trial no | Bleaching agents[b] | Pulps before alkali extraction | | | Alkali-extracted pulps | | |
|---|---|---|---|---|---|---|---|
| | | Kappa number[c] | Intrinsic viscosity (mL/g) | HexA content (meq/kg) | Kappa number[c] | Intrinsic viscosity (mL/g) | HexA content (meq/kg) |
| 1 | Reference[d] | 29.9 | 1188 | 26.4 | 25.9 | 1176 | 25.7 |
| 2 | POM1 | 26.4 | 1098 | 24.0 | 26.7 | 1166 | 24.7 |
| 3 | POM1[e] | 26.9 | 1143 | 25.6 | 25.5 | 1176 | 23.3 |
| 4 | POM2 | 26.3 | 960 | 26.3 | 26.3 | 964 | 25.3 |
| 5 | SiMo | 28.8 | 1127 | 25.2 | 26.6 | 1128 | 24.2 |
| 6 | SiMo & 0.2% $H_2O_2$ | 26.8 | 1068 | 23.2 | 25.5 | 1062 | 21.3 |
| 7 | SiMo & 0.5% $H_2O_2$ | 26.1 | 991 | 19.6 | 24.0 | 994 | 17.4 |
| 8 | POM1 & SiMo | 27.6 | 1123 | 25.0 | 25.6 | 1093 | 23.8 |
| 9 | POM2 & SiMo | 27.6 | 980 | 27.9 | 25.9 | 976 | 25.8 |
| 10 | POM1 & SiMo[e] | 26.9 | 1112 | 24.3 | 25.2 | 1147 | 21.0 |

[a] *Properties of original, unbleached pulp: kappa number 30.0 (not corrected for HexA), intrinsic viscosity 1188 mL/g, HexA content 27.7 meq/kg o.d. pulp.*

[b] *POM1 is $K_6[AlMn^{III}(H_2O)W_{11}O_{39}]$ and POM2 is $(NH_4)_5H_4[PV_6Mo_6O_{40}]$; bleaching conditions (unless otherwise noted): 10% consistency, pH ~5, 90 min, ~90 °C, $p(O_2)$ = 0.5 MPa, [POM] = 0.3 mmol/L (~10 g/kg o.d. pulp), and [SiMo] = 0.6 mmol/L calculated as Mo (~0.5 g/kg o.d. pulp); $[H_3CCOONa]$ = 0.1 mol/L.*

[c] *The kappa numbers are not corrected for HexA.*

[d] *Test run without catalysts.*

[e] *[POM] = 1.5 mmol/L (~50 g/kg o.d. pulp).*

The results in Table 1 show, as expected, best delignification for pulps that were alkali-extracted after the bleaching trials. Evidently, this is due to the fact that the solubility of residual lignin in alkali increases during oxygen bleaching. The biggest kappa number reduction compared to the original, unbleached pulp—6.0 units after alkali extraction—was obtained in trial number 7 (SiMo with 0.5% addition of $H_2O_2$) whereas the biggest kappa reduction—4.8 units—without peroxide addition was seen when pulp was bleached with POM1 and SiMo (trial no. 10) and subsequently alkali-extracted. The viscosity values are high for all of the pulps. Biggest viscosity losses were seen for the pulps bleached with POM2—possible reasons for this will be discussed later.

In addition to the apparent poor selectivity of POM2, other evident differences between the results of the bleaching trials presented in Table 1 are hard to see. This is

due to the obvious poor delignification performance of the catalytic bleaching concept (possible reasons for this are discussed later). In order to make the analysis of the results easier, a statistical parameter *K* for each catalyst treatment was calculated. Mathematically the *K* values were determined as described in Equation 1:

$$K = \sqrt[4]{\kappa_1 \times \kappa_2 \times c_1 \times c_2} \qquad (1)$$

where $\kappa_1$ and $\kappa_2$ are the kappa numbers of the bleached pulps before and after alkali extraction; $c_1$ and $c_2$ are the respective values for HexA content of the pulps. Because in calculating *K* all of the measured bleaching data for each trial were taken into account, gives the parameter a better picture on the efficiency of each catalyst or catalyst combination than any of the kappa numbers or HexA values alone.

In Table 2 the values of the parameter *K* are tabulated with the $\Delta viscosity$ values for each bleaching trial. $\Delta viscosity$ is the mathematical difference between the intrinsic viscosity of the original unbleached pulp and the average intrinsic viscosity values (i.e. before and after alkali extraction) of the bleached pulps.

*Table 2.*
*Bleaching performance of the catalysts presented with statistical parameter K and ⊿viscosity*[a]

| Trial no | Bleaching agents | Δviscosity (ml/ g) | K (a.u.) |
|---|---|---|---|
| 1 | Reference[b] | 6 | 26.9 |
| 2 | POM1 | 56 | 25.4 |
| 3 | POM1[c] | 28 | 25.3 |
| 4 | POM2 | 226 | 26.1 |
| 5 | SiMo | 60 | 26.1 |
| 6 | SiMo & 0.2% $H_2O_2$ | 123 | 24.1 |
| 7 | SiMo & 0.5% $H_2O_2$ | 195 | 21.5 |
| 8 | POM1 & SiMo | 79 | 25.5 |
| 9 | POM2 & SiMo | 210 | 26.8 |
| 10 | POM1 & SiMo[c] | 58 | 24.2 |

[a] *Intrinsic viscosity of the original, unbleached pulp was 1188 ml/ g.*
[b] *Test run without catalysts.*
[c] *[POM] = 1.5 mmol/ l (~ 50 g/ kg o.d. pulp).*

Looking at the results in Table 2 makes the poor selectivity of POM2 very clear: when this catalyst was used (trials 4 and 9) viscosity loss was rather severe (more than 200 units), yet the value of *K* is at the same level with the reference trial (no 1). Earlier works by other authors (*15,20,47,48*) have shown that in catalytic bleaching with $[PV_5Mo_7O_{40}]^{8-}$ and $[SiV_4W_8O_{40}]^{8-}$ anions, in addition to the POMs, also $VO_2^+$ ion acts as a reactive species. Reactions of $VO_2^+$ are unselective and therefore carbohydrates are damaged (*49*). Our observations indicate that an analogous mechanism may well be operative in bleaching with POM2. Thus, the conclusion is that POM2 catalyses more effectively the oxidation of carbohydrates than the oxidation of lignin and HexA. Therefore, POM2 is not suitable for catalytic delignification in the tested conditions.

From Table 2 also some other observations can be made. It is seen that POM1 catalyses oxidation of lignin and HexA to some extent (trials 2 and 3). Moreover, SiMo used together with $H_2O_2$ reacts more effectively with lignin and HexA than SiMo used as

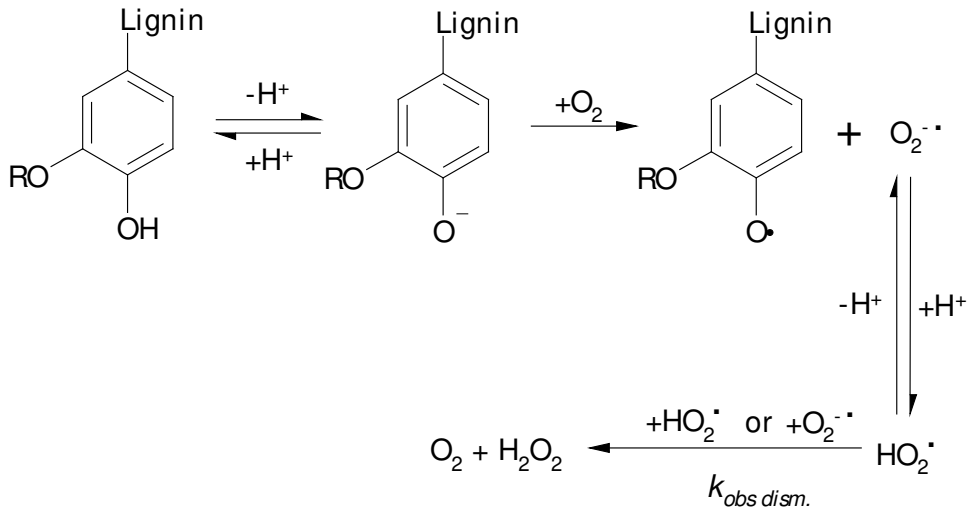
such, in the presence of $O_2$ only—decrease in the value of *K* seems to be directly proportional to the amount of hydrogen peroxide used (comparison of *K* for trials 5, 6 and 7). Finally, it is seen that POM1 used together with SiMo reacts more efficiently with lignin and HexA than POM1 and SiMo used alone (Table 2, trials 2, 3, 5, and 10).

Despite the slight synergistic effect seen in combined usage of POM1 and SiMo, the stark fact concerning the results presented in this paper is that bleaching carried out with our catalytic system is far from being economically viable: in contemporary (non-catalytic) alkaline oxygen delignification processes normally ~50% delignification degree is achieved (*50*). Even when high dosages of catalysts (up to 50 g POM1 in kg o.d. pulp) were used, delignification rates were low. The reason for this is simple: the combined activity of our catalysts is too low. More precisely, it is very probable that the slow reoxidation rate of POMs used in our system is detrimental to delignification—this was already suspected for POM1 in our earlier paper, where simulations of catalytic POM bleaching were carried out (*51*). Fast reoxidation of the POM catalyst is crucial for two reasons: firstly, to ensure effective oxidation of phenolic lignin structures and secondly to enable sufficient generation of radical species that can combine to hydrogen peroxide *in situ* and thus prepare the way for effective SiMo-activated bleaching (see Scheme 1).

According to the reasoning above, it can be postulated that the performance of our catalytic bleaching system could be increased if a catalyst was found that would be effective and selective in lignin oxidation and yet be easily reactivated by $O_2$. Provided a suitable catalyst is found, generating enough $H_2O_2$ *in situ* should not cause any problems—actually $H_2O_2$ production from the radical species is faster at acidic than at alkaline conditions. This view can be backed up with information found in literature, which will be shortly reviewed below.

In alkaline oxygen delignification, the initiation reaction of the radical process is the reaction of $O_2$ with a dissociated (i.e. deprotonated) phenolic lignin structure (*38*,*39*). In this reaction, shown in Scheme 2, a phenoxy radical and a superoxide anion radical are formed. Superoxide radical is the conjugate base of hydroperoxy radical ($pK_a$ = 4.8) (*52*). Thus, in aqueous solution the molar ratios of these radical species depend on pH. Moreover, superoxide and hydroperoxy radicals can combine and through this dismutation reaction hydrogen peroxide is formed (Scheme 2).

*Scheme 2. Some reactions nof oxygen ($O_2$), superoxide anion radical ($O_2^{-\bullet}$), and hydroperoxy radical ($HO_2^{\bullet}$) in oxygen delignification. For further details, see text.*




Clearly, the reactions depicted in Scheme 2 are pH-dependent. Dissociated phenolic compounds are much more susceptible to oxidation by $O_2$ than the undissociated structures (*53*). The $pK_a$ values of phenolic lignin structures vary between 6.2 and 11.3 (*54*); therefore it is advantageous to carry out oxygen delignification at alkaline conditions, where most of the phenolic lignin residues are dissociated. Furthermore, at acidic conditions lignin is not too reactive, which leads to poor delignification (as seen in Table 1, reference bleaching) as well as to low amounts of superoxide produced in lignin oxidation reactions. Quite on the contrary, however, the dismutation reaction (Scheme 2, bottom) is much faster at acidic than at alkaline conditions. This is due to the fact that the reaction rate of two superoxide radicals combining is negligible compared to the reaction rate of a hydroperoxy radical combining with another hydroperoxy radical or with a superoxide radical. It has been reported (*52*) that the dismutation reaction is somewhat $10^5$ times faster at pH 5 compared to pH 10 (the respective $k_{obs\,dism.}$ values are ~$10^7$ L/mol s and ~$10^2$ L/mol s).

Based on the discussion above, two logical assumptions concerning acidic conditions and oxygen delignification can be made:

1) A catalyst is needed to ensure effective oxidation of phenolic lignin structures: at pH < 7 the vast majority of the phenolic groups are not dissociated and thus unreactive towards molecular $O_2$.
2) Free radicals originating from $O_2$ reactions are likely to be present at lower concentrations compared to alkaline oxygen delignification.

Thus, it can be argued that because at acidic conditions the radical species ($O_2^{-\bullet}$ and $HO_2^{\bullet}$) are very rapidly consumed in the dismutation reaction producing hydrogen peroxide, carbohydrate-degrading radical reactions should take place to a lesser extent than at alkaline conditions. Moreover, SiMo activation may play some role in inhibiting radical reactions, as well: $H_2O_2$ is captured by the molybdate polyanions and

decomposition of the peroxide into extremely reactive and unselective hydroxyl radicals (HO˙) is hindered. Some indication of this protection for carbohydrate polymers provided by the consumption of the harmful radicals into SiMo activation can also be seen in our results. When POM1 was used together with SiMo (trial no. 10), selectivity was better than in bleaching trials where SiMo was used together with $H_2O_2$ (trial nos. 6 and 7): $\Delta viscosity$ for trial no. 10 is 58 ml/g while the respective values for trials 6 and 7 are 123 and 195; yet the value for the parameter *K* do not vary much.

## CONCLUSIONS

The results presented in this work showed modest delignification results for a biomimetic catalytic process where POMs $K_6[AlMn(H_2O)W_{11}O_{39}]$ and $(NH_4)_5H_4[PV_6Mo_6O_{40}]$ were used in conjunction with SiMo. Although the results indicate that with the catalysts tested the novel bleaching method has no commercial potential, in some bleaching trials slight synergistic effect in the concomitant use of POM and SiMo catalysts was seen.

The key issue that hindered the delignification reactions in the catalytic bleaching concept can be concluded to be the slow reoxidation rate of the tested POMs. Therefore, in future research, the emphasis should be on finding a redox catalyst that selectively and effectively can, at slightly acidic pH, oxidise phenolic lignin structures and, in addition, is rapidly reoxidised with $O_2$. Finding the optimal catalyst may not be easy, however: a multitude of POMs has been tested during recent years by many researchers as catalysing agents but the inefficient reoxidation has frequently caused problems (*14,25,30,51*). Still, in this context its good to note that the redox catalyst applicable in the reactions depicted in Sceme 1 does not necessarily have to be a POM anion: for example, certain organic quinone compounds are known to oxidise aromatic organic structures (*55,56*).

Finally, it can be concluded that to significantly enhance the performance of the catalytic bleaching concept outlined in this paper will be, to say the least, time-consuming and laborious. Yet, our personal opinion is that the pursuit for finding apt catalysts may well be worthwhile. Namely, should functional catalysts be found, developing the bleaching concept further would be extremely interesting: harnessing the harmful radical species for effective delignification is, without a doubt, an intriguing idea for anybody working with delignification chemistry.

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