

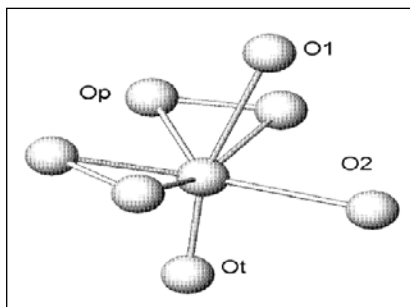
Peroxomolybdate catalysts in pulp hydrogen peroxide bleaching: Improvement in hexeneuronic acid removal and delignification

FABIAN TAUBE, ANDREI SHCHUKAREV, JIEBING LI, GÖRAN GELLERSTEDT, AND ROLAND AGNEMO

ABSTRACT: We have studied the catalytic effects of peroxomolybdates, i.e., $[\text{MoO}(\text{O}_2)_2(\text{OH})(\text{H}_2\text{O})]^-$, on hydrogen peroxide bleaching on hardwood and softwood pulps in terms of kappa number reduction, hexeneuronic acid (HexA) removal, and delignification. We found that, in the case of hardwood pulp, the decrease of HexA in the peroxomolybdate bleaching stage corresponds to more than 60% of the kappa number reduction obtained in that stage. In the case of pine pulp, inclusion of molybdate in the peroxide stage lowered the kappa number by 4.1. This work also shows that hydrogen peroxide, in the absence of molybdate, did not react to any noticeable extent with neither the lignin model compounds or HexA, under otherwise similar conditions. In order to investigate the oxidation mechanism, lignin model compounds with different side chain structures were reacted with peroxomolybdate. $^1\text{H-NMR}$ revealed that lignin model compounds with double bond structure in conjugation with the aromatic ring has an extreme fast speed to react with the peroxomolybdate catalysts systems, presumably through hydroxylation reactions. This mechanism was supported by XPS analysis of the pulp samples, in which the activated hydrogen peroxide was found to act in a similar fashion on surface lignin as well. In conclusion, molybdate activated hydrogen peroxide can be considered a very efficient and selective bleaching agent.

Application: The results in this study add important qualitative information to the results presented in preceding studies that focused on the speciation of peroxomolybdate complexes and on the efficiency of the peroxomolybdate catalyst system.

Diperoxomolybdates are widely used as catalysts in different processes. A major use is in the catalytic epoxidation of olefins[1], but several derivatives of diperoxomolybdates, incorporating organic ligands, are also being used in oxidation of primary and secondary alcohols, epoxides, sulfides, sulfoxides, metal alkyls, etc. (see Kubelka, Francis, and Dence[2] and references cited therein). Recent studies have shown that a catalytic amount of molybdate can be used as an activator for hydrogen peroxide under weakly acidic conditions in the bleaching of paper pulp[3-5]. Furthermore, this highly selective delignification has proven to be more effective by adding phosphate or silicate to the pulp. In a study, amounts of 100 ppm phosphate or silicate were found to increase the bleaching selectivity by 100 viscosity units, given the same Kappa number[6]. The proposed peroxomolybdate catalysts, i.e.,



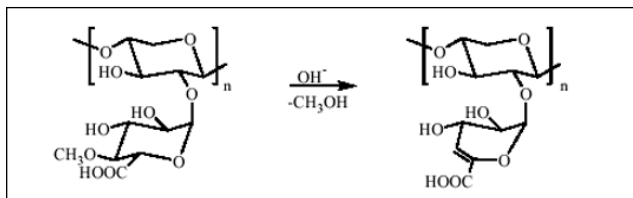
1. Ball and stick model of a diperoxomolybdate anions (hydrogen atoms are omitted), where Op = peroxo oxygens, Ot = double-bonded oxygen, and O1 and O2 = other oxygens (e.g., H_2O or OH^-).

$[\text{MoO}(\text{O}_2)_2(\text{OH})(\text{H}_2\text{O})]^-$, are suggested to consist of one molybdate unit with two peroxogroups attached[7], i.e., as shown in **Fig. 1**.

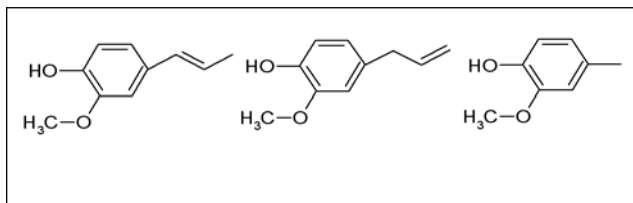
When polymolybdates are being used in redox reactions in which no hydrogen peroxide is present, the molybdenum (VI) ion itself (or an additional transition metal incorporated in the polyanion structure) oxidizes the sub-

strate and thereby becomes reduced. In the case of peroxomolybdates, the catalytic properties originate from the enhanced electrophilic character of the peroxo oxygens[8] that arises when peroxide coordinates to the metal center. Hence, the oxidation state of the metal ion is not altered. Thus, peroxomolybdates can be considered as electrophilic oxidants and are proposed to react through a transfer of peroxide oxygens to the substrate[9]. So far, studies on the redox chemistry behind the delignifying properties of these peroxomolybdate anions have not been investigated. Such information is of great importance in order to understand how these catalysts act on pulp fibres, but also in predicting the optimal conditions for industrial bleaching of pulp.

Previously, it has been found that 4-O-methyl-D-glucuronic acid groups, present in xylan, can be converted into the corresponding unsaturated acid 4-deoxy-L-threo-hex-4-enopyranosyluron-



2. Formation of hexeneuronic acid units from 4-O-methyl-D-glucuronic acid in xylan during alkaline pulping.



3. Structures of isoeugenol (left), eugenol and creosol (right).

ic acid, so called hexeneuronic acid (HexA), during alkaline pulping[10], according to **Fig. 2**. Hexeneuronic acid groups are of interest from a pulp bleaching perspective, since they will interfere with the method of determination of residual lignin, i.e. the kappa number. Furthermore, such structures will have a different reactivity as compared to lignin toward various bleaching agents, and perhaps contribute to a higher demand for bleaching chemicals[11].

In order to elucidate in detail the effect of peroxomolybdate activated bleaching on pulp, concentrations of HexA in birch- and pine pulps at different stages of the bleach process were measured. The bleaching effect could then be described in terms of HexA removal and the true delignification, based on the corrected kappa number, i.e., when the kappa number contribution of HexA has been taken into account.

In an attempt to verify the type and kinetics of reactions involved between the selected peroxomolybdate anions and lignin residuals in the bleaching of wood pulp, specific lignin model compounds were used (**Fig. 3**). Each of these monomeric compounds, isoeugenol, eugenol and creosol, are parts of lignin and consists of a phenol group with or without (creosol) an unsaturated side chain. In addition, the double bond structure in the side chain of isoeugenol is in conjugation with the aromatic ring.

Recent studies on the redoxchemistry of lignin model compounds in peroxomolybdate catalysts systems have shown that the oxodiperoxomolybdenum (VI) complexes abstract an electron from the aromatic nuclei to form radical cations[12-13]. For the ethylguaiacol dimer, a non-phenolic lignin model used in these studies, cleavage of the α - β bond in the side chain was observed, as a result of homolytic fragmentation of these radical cations. Similar results were found for the phenolic monomers used in these studies. None of these monomers however has a double bond structure in the side chain in conjugation with the aromatic ring.

Surface chemical composition of the pulp at different stages of bleaching can be studied by x-ray photon spectroscopy (XPS), which can provide information on the type of oxidation reactions taking place at the surface. The thin layer of

lignin remaining at the surface of the fibre after the kraft cook has been found to be more difficult to remove in the bleaching stage, especially early in the bleaching sequences, than the "internal residual lignin." One of the reasons to this might be the different composition of surface lignin compared to the "internal residual lignin," i.e., low amounts of free phenolic lignin units or high amounts of condensed structures (stable C-C lignin structures)[14].

Surface lignin have been found to play an important part in the development of pulp brightness during bleaching, and have also been suggested to be more colored than the residual lignin in the other regions of fibers[14]. Moreover, the amount of surface lignin have been found to be about five times higher than the amount of lignin in the bulk[15]. Thus, it is of great importance to study the effect of different bleaching agents on surface lignin.

In this study, no attempt has been made to determine the specific amount of lignin at the surface of the pulp. The purpose of the XPS analyses was to study the effects of different bleaching stages on the relative amount of oxygen atoms and various carbon atoms (with different oxidation states) at the fibre surface. From this, conclusions can be drawn upon the type of oxidation reactions taking place at the surface. The reliability of indirectly monitoring the surface lignin content of pulp by means of XPS has been tested previously[16].

MATERIAL AND METHODS

Bleaching and preparation of pulp

Laboratory-made, oxygen pre-bleached (pH~12, 100 °C and 1 hrs), birch and pine kraft pulps (with initial kappa numbers of 10 and 16.6 and viscosities of 881 and 967 cm³/g respectively) were processed through various stages of the bleach process. This process was divided into four stages, beginning with a complexing stage (Q), using 6% EDTA (based on dry pulp weight) at pH~5, 70 °C and 1 hr, followed by an activation stage, using either 10% hydrogen peroxide (P), 10% hydrogen peroxide and 300 ppm molybdate (PMo), or 10% hydrogen peroxide, 300 ppm molybdate and 100 ppm silicate (PMoSi) at pH~5.5, 80 °C and 3 hrs. Sodium dihydrogen phosphate buffer was used in the activation stage, in order to maintain pH at 5.5. Thus, phosphate was always present in this stage. The activation stage was followed by a repeated Q-stage under similar conditions as the initial Q-stage. In the final stage, (EP), 10% peroxide and 10% sodium hydroxide was added under alkaline condition, i.e., at pH~11, 70 °C and 2 hrs. Prior to each bleaching stage, the pulp were washed and centrifuged. Determinations of kappa number were done in accordance with SCAN-C 1:77. A more detailed description of the bleach process can be found in Agnemo[17].

After each stage, pulp was taken out of the process for preparation of pulp sheets, used in the XPS-analyses. The pulp sheets were prepared as "Finnish arc sheets"[6]. The extractives were removed with dichloromethane in a Soxhlet extraction apparatus, according to standard SCAN-C 7:62. Samples from the sheets were clipped to the sample holder. In this

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process, eventual contamination of carbon containing substances was avoided as far as possible. The samples were then set to outgas overnight in the turbo-pumped entry chamber in order to stabilize the water content in the sample matrix.

Quantitative determination of HexA in the pulp

The presence of HexA in the birch pulp and pine pulp after each bleaching stage was determined with a method based on HPLC, developed at the Royal Institute of Technology, Division of Wood Chemistry. A detailed description of the method can be found in Gellerstedt and Li[11].

Preparation of lignin/catalyst mixtures

The aqueous peroxomolybdate and peroxomolybdophosphate solutions were all prepared according to the works of Taube, et. al.[18] and Taube, et. al.[19] at two different pH values, about 3 and 5, and with concentrations similar to those found in the bleach process; that is, approximately 1 mM of molybdate and 40 mM of peroxide. (For the peroxomolybdophosphate solutions, about 10 mM of phosphate.) By using this preparation procedure, precise information on the type and concentration of peroxomylbdate/peroxomolybdophosphate anions present in the solution can be achieved. 10 ml of a molybdate or molybdophosphate solution without peroxide were mixed with 10-20 µl of liquid isoeugenol, eugenol, and creosole, respectively. Each mixture was heated to 80 – 90 °C for about 5 minutes while stirring in order to emulsify the organic phase in the aqueous phase before addition of hydrogen peroxide. After addition of 50-100 µl hydrogen peroxide (30%, Merck *p.a.*) heating and stirring were continued for an additional 5 minutes. The organic phase was then extracted by using ethyl acetate (Labscan *a.r.*). Any remaining water was removed from the organic phase by adding sodium sulphate (Merck *p.a.*). Ethyl acetate was removed by evaporation and the organic phase was then dissolved in acetone (98%, Merck *p.a.*) prior to the ¹H NMR measurements.

¹H NMR measurements

The purpose of the ¹H NMR measurements in the present work was to identify possible oxidation products from reactions of peroxomolybdates and peroxomolybdophosphates with the lignin model compounds mentioned above. Spectra were recorded at 400.14 MHz on a Bruker DPX 400 spectrometer. Chemical shifts are referred to tetramethylsilane (TMS).

XPS analyses

The XPS analyses were performed using a Kratos Axis Ultra spectrometer. Wide spectra (pass energy 160 eV) and spectra of individual photoelectron lines (pass energy 20 eV) were acquired using a monochromatised Al Kα source operated at 180 W. To compensate for surface charging, a low energy electron gun was used. Spectra were processed with Kratos software and the binding energy scale was referenced to the C 1s line of aliphatic carbon, set at 285.0 eV. In several cases, liquid nitrogen cooling of the sample was used to avoid alteration of chemical speciation at the surface due to high vacuum. Mea-

Bleaching stage (BIRCH PULP)	Kappa number (units)	HexA (µmoles/g pulp)	Kappa number equivalence (units)
O ₂ -prebleached	10.0	50.0	4.3
Q+P	8.6	45.1	3.9
Q+P+Q+EP	6.8	45.0	3.9
Q+PMo	5.8	25.8	2.2
Q+PMo+Q+EP	4.3	25.6	2.2
Q+PMoSi	5.9	22.4	1.9
Q+PMoSi+Q+EP	4.3	22.3	1.9

Bleaching stage (PINE PULP)	Kappa number (units)	HexA (µmoles/g pulp)	Kappa number equivalence (units)
O ₂ -prebleached	16.6	23.7	2.0
Q+P	15	22.2	1.9
Q+P+Q+EP	10.4	22.7	1.9
Q+PMo	10.8	14.1	1.2
Q+PMo+Q+EP	6.3	12.9	1.1
Q+PMoSi	10.6	12.0	1.0
Q+PMoSi+Q+EP	6.1	11.7	1.0

I. Kappa number, content of HexA found in pulps and its contribution to the kappa number.

surements were taken at three different spots on each sample in order to average for the heterogeneity of the sample.

Spectra of C1s and O1s were recorded, and the total O/C atomic ratio, and the atomic percent (at%) of different carbons, as indicated by chemical shifts in the C1s peak, were calculated. Deconvolution of the carbon C1s peak was done by fitting Gaussian/Lorentzian (70/30) curves using the curve fitting program supplied by the manufacturer of the spectrometer.

RESULTS

HexA removal and delignification

As shown in Table 1, the amount of HexA in the oxygen prebleached, birch, and pine kraft pulps were determined to 50.0 and 23.7 µmoles/g pulp. Previously, it has been suggested that 10 µmoles of HexA/g pulp contributes to 0.86 kappa units[20]. This implies that the contribution of HexA to the initial kappa number for the birch and pine kraft pulps used in this study corresponds to 4.3 and 2.0 units, respectively. Considering the initial kappa number for the oxygen pre-bleached birch pulp (10.0) the contribution to the kappa number from HexA is substantial, which is not the case for the pine pulp (initial kappa number 16.6)

		Birch pulp						Pine pulp					
		Hydrogen peroxide (P)		PMo		PMoSi		Hydrogen peroxide (P)		PMo		PMoSi	
		P	EP	P	EP	P	EP	P	EP	P	EP	P	EP
Kappa No. reduction	Total kappa No. decrease	1.4	1.8	4.2	1.5	4.1	1.6	1.6	4.6	5.8	4.5	6.0	4.5
Effect on HexA	Kappa No. decrease by HexA	0.4	0	2.1	0	2.4	0	0.1	0	0.8	0.1	1.0	0
Effect on lignin	Kappa No. decrease by lignin*	1.0	1.8	2.1	1.5	1.7	1.6	1.5	4.6	5.0	4.5	5.0	4.5

* subtracting the kappa number decrease of HexA from the total kappa number decrease.

II. Bleaching effects of hydrogen peroxide in terms of kappa number reduction, HexA removal and delignification.

Using the kappa number contribution from HexA, the total decrease in kappa number could be further interpreted into bleaching effects of HexA and the rest as of lignin (**Table 2**).

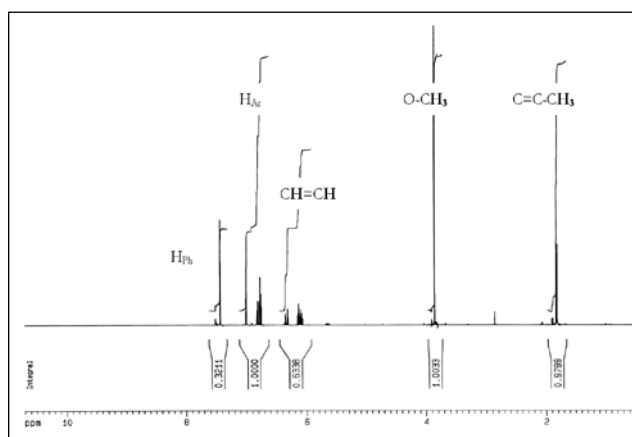
As can be concluded from Table 1, most of the HexA remains in the pulp fibers when the pulps are bleached without addition of molybdate, i.e., through the sequence Q + P + Q + EP. Furthermore, this “non-activated” hydrogen peroxide sequence has limited effects on delignification as well, resulting in a kappa number reduction between 1.4 and 1.6 units (Table 2). It is also clear from Table 1 and 2 that the decrease in kappa number during the alkaline peroxide bleaching stage (EP) is an effect solely by delignification, i.e., there is no decrease in HexA content in the pulp during the EP stage.

Addition of molybdate increases substantially the kappa number reduction, caused both by HexA removal and increased delignification. The content of HexA decreases from 45.1 (Q + P) to 25.8 μ moles/g (Q + PMo) in the birch pulp (Table 1), which correspond to 1.7 kappa units, or more than 60 % of the kappa number reduction obtained in the PMo stage. In the case of pine pulp, the contribution to the kappa number reduction from HexA in the PMo stage is around 19%, i.e., oxidation of HexA accounts for only 0.8 of the 4.1 kappa units reduction in the Q+PMo+Q+EP stage. This indicates that the PMo stage is efficient in oxidizing lignin as well. Moreover, addition of silicate in the activation stage (Q + PMoSi) results in no further kappa number reduction.

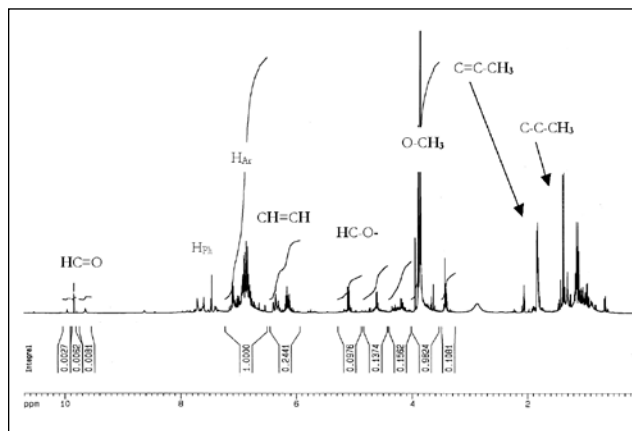
The effect of phosphate could not be measured within this experiment, since phosphate was used as a buffer in the bleaching sequences and therefore present in all pulp samples.

Oxidation reactivity and mechanism with lignin model compounds Isoeugenol:

A ^1H NMR spectrum of isoeugenol is shown in **Fig. 4**. Upon addition of the peroxomolybdate catalyst, the intensity of the signals from protons attached to the double bonded carbons decreases by more than 60 % (**Fig. 5**). The weak signal at $\delta_{\text{H}} \sim 9.8$ ppm arises from protons in aldehyde. The formation of aldehyde indicates broken carbon double bonds. However, the relatively small amounts of aldehydes detected implies that the

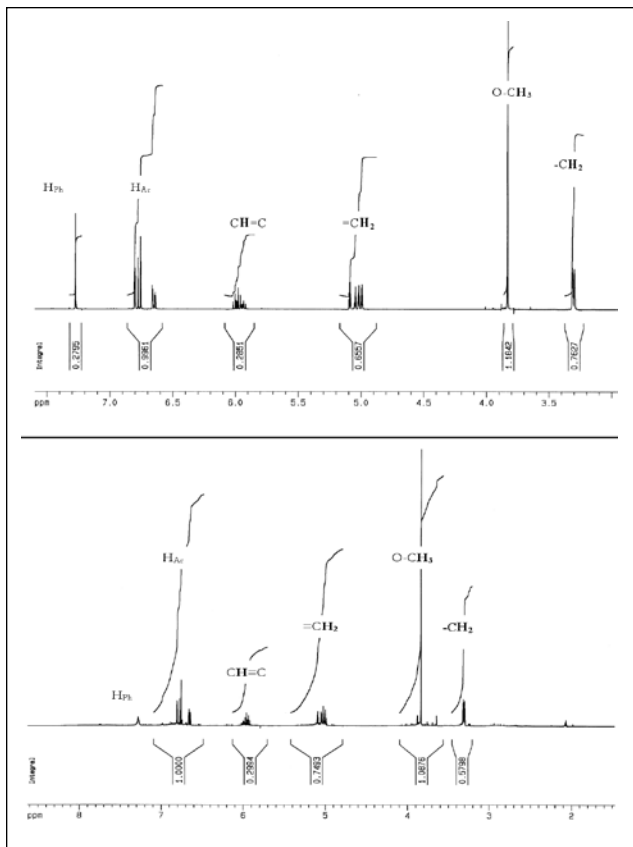


4. ^1H NMR spectrum of isoeugenol. H_{Ph} denotes protons in the phenol structure, H_{Ar} denotes protons in the aromatic structure.



5. ^1H NMR spectrum of the oxidation products from mixing isoeugenol with a peroxomolybdate solution.

double bonds primarily are hydroxylated or epoxidised, rather than completely broken. This is also indicated by the signals in the region 4.6-5.2 ppm, which arise from protons in such environments. Furthermore, the intensity of the signals arising from methyl protons ($\delta_{\text{H}} \sim 1.8$ ppm) also decreases by more than 60%. At the same time, new signals emerge at $\delta_{\text{H}} \sim 1.4$ ppm, which is consistent with hydrogen atoms in a methyl group



6. Top: ^1H NMR spectrum of eugenol. Bottom: ^1H NMR spectrum of the oxidation products from mixing eugenol with a peroxomolybdate solution.

bound to a saturated carbon atom. The signals upfield from the methyl proton signals arises from a mixture of non-identified products. Only very weak signals could be detected in the range δ 10-15 ppm, indicating that almost no acidic groups, such as carboxylic groups, have been formed. This clearly suggests that the aromatic ring in isoeugenol is mainly left intact. A fourfold increase in the peroxide concentration (to 160 mM) did not result in higher yield, while lowering the pH-value in the aqueous solution from 5 to about 3 resulted in a somewhat lower yield of products. However, the latter effect might be caused by a lower solubility of isoeugenol at pH $\sim$ 3. The reaction of hydrogen peroxide alone, in the absence of molybdate, was also studied by adding isoeugenol to a solution containing 40 mM hydrogen peroxide at pH $\sim$ 3, under otherwise identical conditions as above. As expected, only very small amounts of products were detected.

The effect of adding phosphate to the aqueous solution was also investigated. Isoeugenol was added to a solution containing a mixture of diperoxomolybdophosphate and diperoxomolybdate at pH $\sim$ 5, i.e., in accordance with the concentrations and pH used in industrial bleaching with peroxomolybdate anions. However, the type and yield of products were found to be very similar to those in the absence of phosphate.

Eugenol and creosol

As can be seen from **Fig. 6**, the addition of eugenol to a peroxomolybdate solution did not result in any noticeable change in the ^1H NMR spectra. It thus seems that the conjugated aliphatic carbon double bond in isoeugenol can be oxidized, while the non-conjugated aliphatic double bond in eugenol is unaffected. The creosol molecule, containing no unsaturated side chain, was also mainly left intact.

Surface analysis of kraft pulp fibers

Table 3 summarizes the effect of the different bleaching stages on the surface chemical composition of the extracted birch- and pine pulp sheets. As can be seen, there is a decrease in the at% of the aliphatic carbons (C1) as the bleaching proceeds, indicating that the surface content of lignin decreases during the bleaching. This is also indicated by the increase in the O/C atomic ratio during the bleaching stages. Furthermore, there is no significant change in the at% of C-O (C2), and only a relatively small increase in O=C-O (C4), which gives some support for the findings by the ^1H -NMR studies on lignin model compounds, in that the oxidation of aromatic structures with free phenolic groups is negligible, i.e., the formation of carboxylic acid groups is very small. Furthermore, there seems to be no formation of carbonyl groups (or O-C-O, C3) during the bleaching stages. This is also in line with the findings by ^1H -NMR, because the production of carbonyl groups is a clear indication on complete cleavage of conjugated double bonds in the side chains[22]. From the studies on lignin model compounds, it was suggested that these conjugated double bonds was hydroxylated or epoxidised, rather than being completely cleaved.

Although XPS is not an idealistic technique for detailed structural studies on fiber surfaces, the results from the surface analysis indicates that the prevailing oxidation reaction is hydroxylation, rather than epoxidation. This is illustrated by the clear decrease in the C-O_x/O atomic ratio shown in Table 2. In the case of prevailing epoxidation reactions, one would expect the C-O_x/O atomic ratio to increase since the C:O ratio in epoxides is 2:1.

DISCUSSION

From the study on lignin model compounds in the present work, molybdate activated hydrogen peroxide can be considered as an efficient and selective bleaching oxidant, acting initially on conjugated aliphatic carbon-carbon double bonds, through hydroxylation. The double bond structure in conjugation with aromatic ring, i.e., in isoeugenol, has an extreme fast speed to react with the peroxomolybdate catalysts systems (more than 60% reaction yield in 5 minutes reaction time). This is in line with the general classification of hydrogen peroxide (P) as acting on certain functional groups in lignin structures, including different aliphatic double bonds[22]. However, the activation with molybdate increases the efficiency of the peroxide bleaching profoundly. It is be-

Bleaching stage (BIRCH PULP)	O/C	C1 %	C2 %	C3 %	C4 %	C-O _x /O
Lignin [21]	0.34	26.8	43.8	2.1	1.7	1.86
O ₂ -prebleached	0.6	6	44	12	0.5	1.5
Q+PMo	0.64	5	44	11	0.8	1.44
Q+PMo+Q+EP	0.65	4	44	11	0.8	1.43
Q+PMoSi	0.65	4	44	11	0.6	1.41
Q+PMoSi+Q+EP	0.66	4	44	11	0.7	1.41

Bleaching stage (PINE PULP)	O/C	C1	C2	C3	C4	C-O _x /O
O ₂ -prebleached	0.59	8	43	11	0.7	1.47
Q+PMo	0.61	7	43	11	0.9	1.44
Q+PMo+Q+EP	0.64	5	45	11	0.7	1.43
Q+PMoSi	0.63	6	43	11	0.8	1.42
Q+PMoSi+Q+EP	0.65	5	45	11	0.5	1.42

III. The oxygen/carbon atomic ration (O/C) and the atomic percent (at%) of carbons at different oxidation states. C-O_x is calculated as the sum of C2+C3+C4.

lied that the catalytic oxidation reactions could take place at slower rates toward aromatic rings or non-conjugated double bond systems, like creosol and eugenol. This has been studied thoroughly in Manning, et. al.[12] and Ashishkumar and Jain[13], in which the oxidation of lignin models by peroxomolybdate catalysts was still substantial after longer reaction times and in mixed aqueous/organic solvents.

We believe that direct lignin reaction is of considerable importance since it generates radicals and start radical chain reaction toward lignin via carbon centered radical. A fast reaction with isoeugenol is equivalent with a fast starting up of radical chain reaction. This implies that isoeugenol, and/or other double bond structure conjugated with an aromatic ring, could function as a catalyst/activator to start up the initial reaction, leading to break down of non-phenolic lignin structures.

Although the types of reactions responsible for the decrease of HexA in pulp bleached with peroxomolybdate were not investigated, the result from this study suggests that HexA is practically uncreative toward hydrogen peroxide under the present conditions (at pH~5 and in the absence of molybdate, peroxide alone seems to have some effect on the degradation of HexA, al-

though very limited, as shown in Table 1). This indicates that the reaction on HexA by the system relies on radical chain reactions as well, probably demanding the carbon centered radical. Thus, the catalyst function from isoeugenol may also be important for HexA elimination by the system. Therefore, it seems possible that the types of reactions prevailing for the oxidation of the lignin models, i.e., hydroxylation, can explain the degradation of HexA, which consists of conjugated aliphatic C=C and C=O bonds (Fig. 3).

Since HexA can be easily degraded under acidic conditions, it cannot be completely ruled out that the degradation of HexA found in this study to some extent depends on acid hydrolysis. This is however unlikely since the condition used in the activation stage is only weakly acidic (pH~5.5), but also since acid hydrolysis of HexA would have been detected in the Q+P bleaching sequence at pH 5.5, i.e., without the addition of molybdate. From Table 1 it is clear that the majority of HexA in the pulp remains after this sequence.

The positive effect on the bleachability found by adding silicate or phosphate to a peroxomolybdate solution[6] might be explained by the fact that the peroxo (O-O) bond strength in the peroxomolybdate molecule alters as a conse-

quence of the coordination of another ligand, i.e., in a similar fashion as it alters in free hydrogen peroxide when the peroxide group coordinates to a molybdate anion. It has been shown that the oxidizing ability of monomeric diperoxometallates depends largely upon the strength of the O-O bond, i.e., anions with weaker O-O bonds generally are more reactive as oxidizing agents[23-24]. Apart from the type of transition metal, the O-O bond strength was also found to be dependent on the nature of the other coordinated ligands. Griffith[25] has for example shown, by means of FTIR, that the O-O bond length increases on increasing the electronegativity on the molybdenum atom by attachment of fluoride. In general terms, this implies that the more electronegative ligand that coordinates to the peroxomolybdate molecule, the more reactive as oxidizing agent this molecule will be. However, in the case of phosphate, the coordination to peroxomolybdates is relatively weak, i.e., the resulting peroxomolybdophosphate complexes are present only in very low concentrations under the conditions used during bleaching[19].

Finally, it should be stressed that the pulps used in this work were bleached under factory conditions. Under optimal conditions, i.e., longer residence time in the different bleaching stages, an additional decrease of about 2 kappa units can be expected for both birch- and pine pulp[6]. Presumably, increased residence time will not alter the type of reactions prevailing in the bleach stage, but enhance the efficiency of these reactions.

CONCLUSIONS

From the study on lignin model compounds in the present work, molybdate activated hydrogen peroxide was found to act preferably on conjugated aliphatic carbon-carbon double bonds, presumably through hydroxylation. Furthermore, the combined results from XPS and ¹H-NMR in this study indicated that activated hydrogen peroxide acts in a similar fashion on surface lignin as well. Finally, it was found that activated hydrogen peroxide also results in a sub-

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stantial degradation of HexA units, as compared to “non-activated” hydrogen peroxide. In conclusion, molybdate activated hydrogen peroxide can be considered as a selective and efficient delignification and HexA removal agent. **TJ**

FUTURE WORK

Additional catalytic studies on isolated residual lignin, in particular detailed molecular and kinetic studies on the reaction with conjugated systems, would be of interest in order to further reveal the chemistry behind the initial steps.

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INSIGHTS FROM THE AUTHORS

This study gives novel, complementary qualitative information on the type of chemical reactions occurring between well characterized peroxomolybdate catalysts and certain lignin model compounds.

The equilibrium studies on the peroxomolybdate catalysts (published elsewhere) used in the present paper were the most difficult and time consuming part of the research project. Methods used was NMR, potentiometry, and FTIR.

¹H-NMR proved to be particularly useful. ¹H-NMR revealed that lignin model compounds with double-bond structure in conjugation with the aromatic ring react very quickly with the peroxomolybdate catalysts systems.

The study provides important information on the selectivity of hthsis system, which can

be valuable in situations where a combination of bleaching steps are being used. Future studies in this area might add to our knowledge of the mechanisms behind the reaction with certain lignin compounds.

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