Analysis of products from the oxidation of technical lignins by oxygen and $H_3PMo_{12}O_{40}$ in water and aqueous methanol by size-exclusion chromatography

Tobias Voitl, Marina V. Nagel and Philipp Rudolf von Rohr*

Institute of Process Engineering, ETH Zürich, Zürich, Switzerland

*Corresponding author.
 Institute of Process Engineering,
 ETH Zürich, Sonneggstrasse 3,
 CH-8092 Zürich, Switzerland
 Phone: +41-44-632-4388
 Fax: +41-44-632-1325
 E-mail: vonrohr@ipe.mavt.ethz.ch

Abstract

One kraft lignin and two lignosulfonates were oxidized in aqueous acidic solutions containing a polyoxometalate (POM). The degradations were carried out in H_2O or MeOH/H_2O mixtures in the presence of oxygen. The treatment with aqueous $H_3PMo_{12}O_{40}$ led to the dissolution of the studied lignins in the acidic medium (pH 1–2) and to the formation of up to 6.5 wt% vanillin and 6.2 wt% methyl vanillate based on the weight of dry lignin. The lignin oxidation products were analyzed by size-exclusion chromatography (SEC). For this purpose, a SEC method was developed, which allows the analysis of kraft lignin, lignosulfonates, and reaction products thereof without the need to remove the homogeneous catalyst. This method allows the direct observation of depolymerization and repolymerization reactions and hence the provision of a tool for studying the underlying chemistry. It has been demonstrated that the depolymerization of kraft lignin in water is accompanied by counterproductive condensation reactions. These repolymerization reactions were effectively prevented by addition of methanol, which couples competitively with lignin intermediates.

Keywords: condensation; kraft lignin; lignosulfonates; methanol; oxidation; oxygen; polyoxometalate; size-exclusion chromatography (SEC).

Introduction

Wood consists of approximately 40–50% cellulose, 15–30% lignin, 15–25% hemicelluloses, and 1–10% extractives. Lignin, being the second most abundant component in biomass, represents an alternative feedstock for the production of aromatics (Goheen 1981). Wood sawdust may directly be utilized to produce a variety of basic chemicals including aromatics derived from natural lignin. However, technical lignins obtained as byproducts from chemical pulping processes represent a more immediately accessible feedstock. The two most prominent pulping processes, kraft pulping and sulfite pulping, provided approximately 120 million tons of kraft pulp and 5.7 million tons of sulfite pulp in 2005 worldwide (Auhorn and Niemela 2007). Hence, approximately 72 million tons of kraft lignin and 3.4 million tons of lignosulfonates accrue in the spent liquor annually. Typically, the spent liqours are concentrated and delivered to a recovery furnace in which lignin is combusted and utilized for the generation of steam. Although recovery of technical lignins from spent liqours is possible by precipitation or membrane filtration at relatively low cost, virtually no kraft lignin and only a very small fraction of lignosulfonates are extracted from the pulping processes for economic reasons. Only a few low-value applications (e.g., lignosulfonates as dispersants in concrete admixtures) for technical lignins exist and the breakthrough for processes that convert kraft lignin into higher value base chemicals is still pending.

A variety of thermal and chemical treatments for the depolymerization of natural and technical lignins have been explored so far (Amen-Chen et al. 2001). Catalytic hydrocracking is commonly referred to as a potential way to convert lignin into liquid chemicals. Herein, lignin is degraded at elevated temperature ($\sim$350–450°C) under reductive conditions ($\sim$80–180 bar H_2) in the presence of hydrogenation catalysts (e.g., Pd, sulfided NiMo) and, optionally, in hydrogen-donating solvents (Meier et al. 1992; Dorrestijn et al. 1999). Typically, catalytic hydrocracking of lignin leads to the formation of a lignin-derived oil in yields up to 80 wt%. Approximately one-third of the lignin-derived oil consists of a broad mixture of monomers. The yield of single monomeric products is relatively low with phenol (1–4 wt%) and cresols (2–5 wt%) being most abundant. This approach aims at the production of a phenolic oil that might be utilized for the production of bulk chemicals.

Alkaline oxidation of lignin represents the only approach that yields reasonably large amounts of single monomeric aldehydes. Vanillin is the only major product from oxidation of softwood lignins, whereas oxidation of hardwood lignins yields a mixture of vanillin and syringaldehyde according to the chemical structure of lignin (Hocking 1997). The yield of aldehydes, however, is sensitive to the source and accordingly to the pretreatment of lignin. Whereas vanillin is commercially produced by oxidation of lignosulfonates in spent sulfite liquors at a yield of approximately 10%, kraft lignin

is not a suitable raw material due to the significantly lower yields that can be obtained from this material (Villar et al. 2001).

We have recently reported a novel approach for the utilization of kraft lignin as an alternative source for the production of vanillin and methyl vanillate (Voitl and Rudolf von Rohr 2008). It is based on the oxidation of lignins in acidic aqueous solution with oxygen in the presence of a polyoxometalate ($H_3PMo_{12}O_{40}$) as a homogeneous catalyst and on the addition of reactants that prevent lignin-lignin coupling reactions. The treatment led to the dissolution of kraft lignin in the acidic media (pH 1.2) and to a maximum yield of 5.18% monomers. Based on the analysis of monomeric products by GC/MS, we have shown that methanol is incorporated into the lignin-derived product methyl vanillate and we have suggested that simple alcohols may prevent acid induced condensation of lignin. However, at this point only monomeric products could be quantified by GC/MS leaving the major part of the product mixture unidentified.

In the present paper, the development of a size-exclusion chromatography (SEC) method will be reported aiming at the analysis of technical lignins and lignin-derived products. This method will be applied to study the chemical changes of technical lignins during oxidation in acidic media. Furthermore, the optimal conditions will be reported, which resulted in maximum yields of 12.7% and 8.8% of monomers from the oxidation of lignosulfonates and kraft lignin, respectively. Based on the literature and our chemical analysis, the main reactions within the studied system will be discussed.

Experimental

All lignin oxidations reported in Table 1 and in Figure 1c–f were conducted in a 50-ml autoclave equipped with a glass liner and internals made of titanium (Parr Instrument Company). First, the aqueous solvent system was prepared in the glass liner. Typically, 0.912 g or 1.825 g of $H_3PMo_{12}O_{40} \times H_2O$ was dissolved in 10 ml or 20 ml solvent (H_2O or MeOH/H_2O) giving a nominal polyoxometalate (POM) concentration of 0.05 mol l^{-1} based on the formula weight of $H_3PMo_{12}O_{40}$ in every experiment. The pH of the solution was measured and ranged between pH 1.1 and pH 1.2. In experiments without POM, the pH was adjusted to the same range by addition of a few drops of mineral acid (HCl or H_2SO_4). The glass liner was placed into the reactor, followed by addition of powdery lignin (100 mg or 200 mg) resulting in a lignin concentration of 10 g l^{-1}. The reactor was sealed and purged 3 times with O_2 and then filled to a pressure of 5 bar or 10 bar corresponding to 1.3 g or 4.0 g of oxygen per g of lignin, respectively. The mixture was heated up to 170°C at a rate of 12 K min^{-1} under stirring at 600 rpm with a gas entrainment impeller. After keeping the reactants at 170°C for 20 min, the heating jacket was removed and the reactor was allowed to cool down to 30°C. After depressurization, the content of the glass liner was poured into a beaker followed by rinsing the glass liner and stirrer with water for a lossless collection of the sample. Quantification of monomeric products (Table 1) was done by extraction with chloroform and GC/MS analysis as described previously (Voitl and Rudolf von Rohr 2008). For SEC analysis (Figure 1) the sample was brought to pH 12 by addition of NaOH$_{aq.}$ and diluted to a concentration of 2 g l^{-1}. Making the sample alkaline serves two purposes: on the one hand, the Keggin structure of the catalyst $[PMo_{12}O_{40}]^{3-}$ degrades at a pH > 2 and is fully decomposed into its precursors $[MoO_4]^{2-}$ and $[PO_4]^{3-}$ at pH 12 (Jurgensen et al. 1992). Destroying the catalyst $H_3PMo_{12}O_{40}$, which is a very strong oxidant, is necessary to prevent any unwanted interaction with the SEC equipment and lignin-derived products. On the other hand, making the solution alkaline assures the complete dissolution of lignin and lignin-derived products, which is a prerequisite for the SEC analysis.

The lignin oxidations reported in Figure 1a,b were conducted in a 400-ml titanium autoclave (PREMEX AG, CH-Lengnau). A 100-ml solvent (H_2O or 80 vol% MeOH/H_2O) was adjusted to pH 1.1 by addition of 35 wt% HCl$_{aq.}$ and poured into the reactor. Then, 5 g of lignin was added and the reactor was sealed and purged three times with O_2 or N_2

Table 1 Yield of monomeric products from oxidation of lignin.

| Acid | Lignin | Solvent (ml) | | O_2/lignin (g g^{-1}) | Yield of monomeric products (wt%) | | |
		H_2O	MeOH		Vanillin	Methyl vanillate	Total
H_2SO_4	Kraft	20	0	1.3	1.18	0	1.18
H_2SO_4	Kraft	4	16	1.4	1.61	1.16	2.76
$H_3PMo_{12}O_{40}$	Kraft	20	0	1.3	2.45	0	2.45
$H_3PMo_{12}O_{40}$	Kraft	4	16	1.4	2.72	2.46	5.18
HCl	Kraft	10	0	4.0	2.77	0	2.77
HCl	Kraft	2	8	4.0	4.96	2.21	7.17
$H_3PMo_{12}O_{40}$	Kraft	10	0	4.0	5.86	0	5.86
$H_3PMo_{12}O_{40}$	Kraft	2	8	4.1	4.61	4.18	8.79
$H_3PMo_{12}O_{40}$	Borresperse	10	0	4.0	5.48	0	5.48
$H_3PMo_{12}O_{40}$	Borresperse	2	8	4.0	5.12	4.91	10.03
$H_3PMo_{12}O_{40}$	Ultrazine	10	0	4.0	6.59	0	6.59
$H_3PMo_{12}O_{40}$	Ultrazine	2	8	4.0	6.47	6.23	12.70
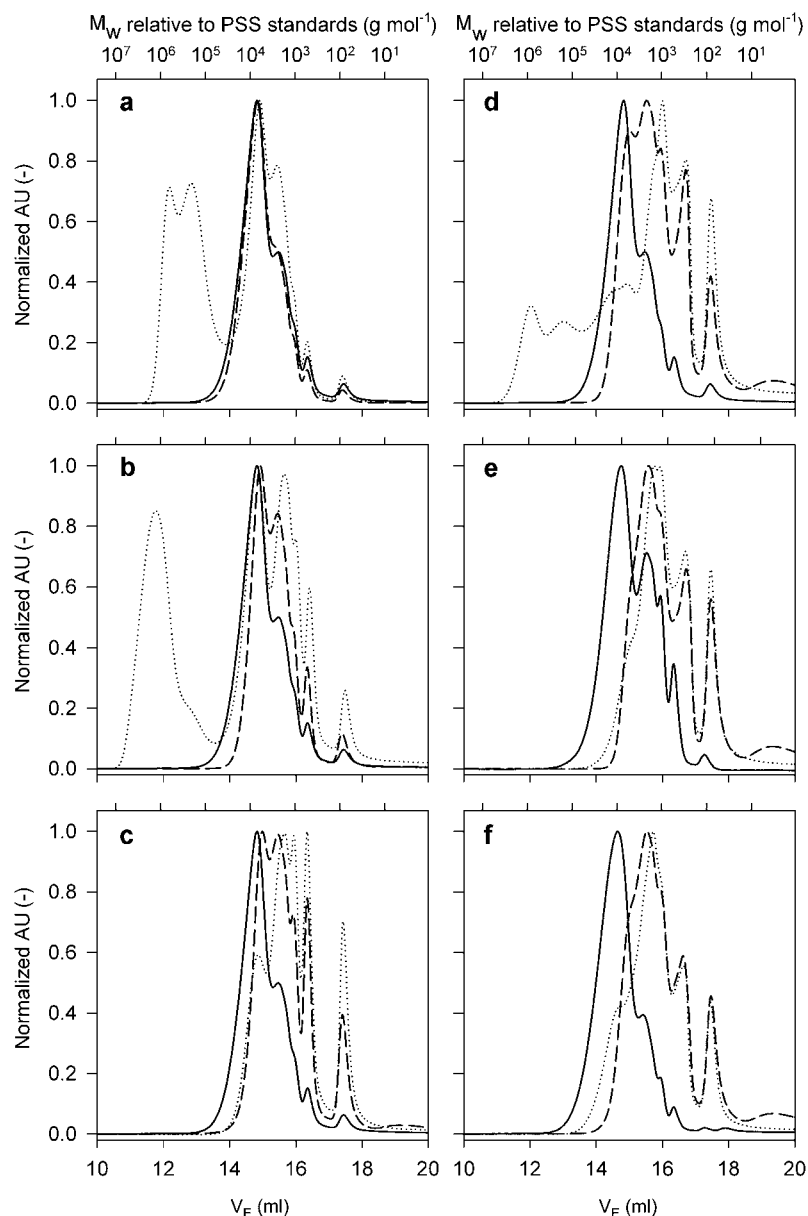
Figure 1 SEC analysis of lignins and lignin oxidation products. Solid lines: untreated lignin. Dashed lines: product from oxidation of lignins in 80 vol% MeOH/H$_2$O. Dotted lines: product from oxidation of lignins in 100 vol% H$_2$O. (a) Kraft lignin, no POM, O$_2$/lignin$=0$ g g^{-1}; (b) kraft lignin, no POM, O$_2$/lignin$=0.4$ g g^{-1}; (c) kraft lignin, no POM, O$_2$/lignin$=4$ g g^{-1}; (d) kraft lignin, POM, O$_2$/lignin$=4$ g g^{-1}; (e) Borresperse, POM, O$_2$/lignin$=4$ g g^{-1}; (f) Ultrazine, POM, O$_2$/lignin$=4$ g g^{-1}.

and then filled to a pressure of 5.5 bar with O$_2$ or to a pressure of 10 bar with N$_2$. The mixture was heated up to 170°C at a rate of 8 K min^{-1} under stirring at 1200 rpm with a gas entrainment impeller. After keeping the reactants at 170°C for 20 min the reactor was cooled down to 30°C. The sample was collected and neutralized with 5 mol l^{-1} NaOH$_{aq.}$ to pH 7. The solvent was removed in a rotavap (Büchi, CH-Uster) and the powdery product was dried in a vacuum oven at 70°C for at least 24 h. Then, 6 mg of the dried product was dissolved in 3 ml of 0.01 mol l^{-1} NaOH$_{aq.}$ for SEC analysis.

SEC was performed on a Waters Alliance 2695 Separations Module equipped with a cascade of SEC columns from Polymer Standards Service GmbH [MCX 10 μm 1000 Å, 100 000 Å (8×300 mm)+precolumn] and a photodiode array detector (UV range 210–400 nm). The eluent (0.01 mol l^{-1} NaOH$_{aq.}$) was freshly prepared from FIXANAL® cartridges, stored under N$_2$ sparging and used for a maximum of 24 h to avoid CO$_2$ uptake. The columns were operated at 35°C and at a constant flow rate of 0.5 ml min^{-1}. Lignin and lignin-derived products were injected at a concentration of 2 g l^{-1} with an injection volume of 5 μl.

Product mixtures from the oxidation of lignins with H$_3$PMo$_{12}$O$_{40}$ contain relatively large amounts of the degraded catalyst. Instead of removing these anions prior to SEC

analysis, we have developed a method allowing direct SEC analysis. A UV wavelength of 320 nm was chosen for the analysis of lignins, because virtually no signal was obtained from the degraded catalyst at this wavelength. Lignin, by contrast, provided a signal at 320 nm, which corresponds to the wavelength reflecting the concentration of aromatic carboxylic acids and α-carbonyl groups (Bikova et al. 2004). Hence, a certain error can be expected if the oxidation leads to the formation of additional carbonyl groups preferably in a fraction of the product mixture. It was assured that the presence of the degraded catalyst does not influence the separation of lignin compounds by fractionation of eluted analyte and its reinjection. It has been shown previously that associative interactions between lignin molecules in $NaOH_{aq.}$ affect the apparent molecular weight distribution (Sarkanen et al. 1984). However, these effects are small at low lignin concentrations and can be neglected in comparison to the effects presented in this work. Also, adsorption of lignin on the column can be excluded, because the material of the columns consists of a sulfonated styrene-divinylbenzene copolymer network. Under alkaline conditions lignin possesses negatively charged groups (phenolate or sulfonate) and does not adsorb on the sulfonated column material due to repulsion. The calibration was done with 9 poly-(styrenesulfonate) sodium salt (PSS) standards with low dispersity in the range of 1 020 000–3420 g mol^{-1}. The position of monomeric species in the chromatogram was determined with vanillin (152 g mol^{-1}) at an elution volume (V_E) of 17.4 ml. The calibration curve obtained with PSS standards reads a molecular weight of 94 g mol^{-1} at $V_E = 17.4$ ml and thus matches well in the low molecular weight region.

Monomeric species were excluded from the calculation of the weight average molecular weight (M_w), the number average molecular weight (M_n), and the polydispersity index ($PDI = M_w/M_n$). The SEC analysis of kraft lignin relative to PSS standards showed slightly higher values of M_w, M_n, and PDI than the values reported for typical kraft lignins (Jacobs and Dahlman 2000).

All chemicals were used as received: kraft lignin (Aldrich 471003), sodium lignosulfonate Ultrazine NA (Borregaard Industries Ltd.), calcium lignosulfonate Borresperse CA (Borregaard Industries Ltd.), $H_3PMo_{12}O_{40} \times H_2O$ (Fluka 79563), $CHCl_3$ (J.T. Baker 7386), CH_3OH (Fluka 65543), H_2SO_4 (Fluka 84720), NaOH (FIXANAL® Sigma-Aldrich 38227), HCl (Sigma-Aldrich 258148). N_2 and O_2 were supplied from PanGas.

Results and discussion

Oxidation of technical lignins in acidic aqueous media yields vanillin and methyl vanillate as the two main monomeric products. Table 1 summarizes the major effects on the yield of these monomers observed in our degradation studies. Methyl vanillate is only obtained if the reaction is carried out in MeOH/H_2O. Methanol as a cosolvent generally results in an increase of the total yield of monomers. This effect is most pronounced in the oxidation of lignins in the absence

of $H_3PMo_{12}O_{40}$. Conducting the reaction in the presence of $H_3PMo_{12}O_{40}$ further increases the yield of monomeric products. Furthermore, it was found that an oxygen to lignin ratio of approximately 4 g g^{-1} initially present in the batchwise oxidation yields to a maximum of 8.8 wt% monomeric products from kraft lignin. Even higher yields can be obtained from lignosulfonates with a maximum yield of 12.7 wt% for the oxidation of an ultrafiltrated lignosulfonate sodium salt (Ultrazine). However, more than 80 wt% of the lignin-derived products are still of higher molecular weight, and conclusions concerning the degradation process are difficult to make solely based on the analysis of monomeric products. Hence, degradation products have been analyzed with SEC and these results are depicted in Figure 1. In each subfigure (a–f) three chromatograms are presented: one of an untreated lignin and two oxidation products thereof, whereas one oxidation product was obtained in H_2O as a solvent and the other was obtained in 80 vol% MeOH/H_2O. A determination of the corresponding average molecular weights and polydispersity indices in relation to PSS standards is presented in Table 2. For a comparison of GC/MS and SEC analysis, identical experimental conditions were applied for the experiments reported in Figure 1c–f and Table 1 (last 8 entries).

First, the treatment of kraft lignin in H_2O at pH 1.1 was studied in the absence of the catalyst under nitrogen and under oxygen (dotted plots in Figure 1a–c). Conducting the reaction under nitrogen did not result in a significant degradation of kraft lignin (Figure 1a). Contrarily, polymerization reactions seem to be the dominating reactions, because a fraction of compounds is formed possessing a higher molecular weight than the original kraft lignin. Addition of a low amount of initial oxygen (O_2/lignin = 0.4 g g^{-1}) led to the formation of degradation products (Figure 1b). However, also a larger amount of products with high-molecular weight are generated, which results in a highly heterogeneous product mixture as reflected by a PDI of 240 (Table 2). The addition of a higher amount of oxygen (O_2/lignin = 4 g g^{-1}) further intensified the formation of products with high-molecular weight, because a large portion of the lignin-derived product remained undissolved after the reaction. The powdery solid did not even dissolve after adjustment of the pH to a value of 12. The yield of solid was determined gravimetrically and reached almost 65 wt% based on the amount of dry kraft lignin. Thus, the chromatogram in Figure 1c shows only the soluble part of the lignin-derived product, which consists of monomeric, dimeric, and oligomeric compounds. For a reasonable analysis by SEC, the analyte needs to be completely soluble in the mobile phase. Hence, determination of the average molecular weight is not applicable for this experiment. Products obtained from all other experimental conditions depicted in Figure 1 were completely soluble at pH 12.

Figure 1d shows analysis of kraft lignin and its products derived from oxidative treatment in the presence of $H_3PMo_{12}O_{40}$ at an O_2/lignin ratio of 4 g g^{-1}. Unlike in oxidations of kraft lignin without the POM in H_2O, the lignin-derived products were completely soluble at pH 12. So,

Table 2 SEC analysis of treated and untreated lignins.

Graph in Figure 1	Plot	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI[a]	Experimental conditions
(a)	Untreated	9460	2790	3.4	Kraft lignin, no POM, O$_2$/lignin=0 g g^{-1}
	80% MeOH	8300	3250	2.6	Kraft lignin, no POM, O$_2$/lignin=0 g g^{-1}
	100% H$_2$O	172 670	4350	39.7	Kraft lignin, no POM, O$_2$/lignin=0 g g^{-1}
(b)	Untreated	9460	2790	3.4	Kraft lignin, no POM, O$_2$/lignin=0.4 g g^{-1}
	80% MeOH	4740	1970	2.4	Kraft lignin, no POM, O$_2$/lignin=0.4 g g^{-1}
	100% H$_2$O	571 040	2380	239.9	Kraft lignin, no POM, O$_2$/lignin=0.4 g g^{-1}
(c)	Untreated	9460	2790	3.4	Kraft lignin, no POM, O$_2$/lignin=4 g g^{-1}
	80% MeOH	4070	1430	2.8	Kraft lignin, no POM, O$_2$/lignin=4 g g^{-1}
	100% H$_2$O	n/a	n/a	n/a	Kraft lignin, no POM, O$_2$/lignin=4 g g^{-1}
(d)	Untreated	9460	2790	3.4	Kraft lignin, POM, O$_2$/lignin=4 g g^{-1}
	80% MeOH	3370	990	3.4	Kraft lignin, POM, O$_2$/lignin=4 g g^{-1}
	100% H$_2$O	140 830	1050	134.1	Kraft lignin, POM, O$_2$/lignin=4 g g^{-1}
(e)	Untreated	10 240	2430	4.2	Borresperse, POM, O$_2$/lignin=4 g g^{-1}
	80% MeOH	2170	830	2.6	Borresperse, POM, O$_2$/lignin=4 g g^{-1}
	100% H$_2$O	2450	750	3.3	Borresperse, POM, O$_2$/lignin=4 g g^{-1}
(f)	Untreated	19 910	4400	4.5	Ultrazine, POM, O$_2$/lignin=4 g g^{-1}
	80% MeOH	2940	970	3.0	Ultrazine, POM, O$_2$/lignin=4 g g^{-1}
	100% H$_2$O	4730	1040	4.5	Ultrazine, POM, O$_2$/lignin=4 g g^{-1}

[a]PDI, polydispersity index (M_w/M_n).

employing $H_3PMo_{12}O_{40}$ as a catalyst in the oxidation of kraft lignin did not only yield increased amounts of monomers but also prevented the formation of insoluble products with high-molecular weight in oxidations in H$_2$O.

Then, the effect of adding methanol to the reaction media was studied (dashed plots in Figure 1). No fraction with high-molecular weight was found in any experiment conducted with 80 vol% MeOH/H$_2$O as solvent, and a higher reduction of the average molecular weight is obtained with increasing O$_2$/lignin ratios (Figure 1a–c, Table 2). The most advanced fragmentation of kraft lignin was obtained at an O$_2$/lignin ratio of 4 g g^{-1} in combination with the catalyst. Whereas GC/MS analysis of monomeric products already showed these trends, SEC analysis undoubtedly revealed that kraft lignin is indeed depolymerized substantially with a maximal reduction of the weight average molecular weight from 9460 g mol^{-1} to 3370 g mol^{-1} at a constant PDI of 3.4.

The effect of POM addition can be judged by comparison of the SEC analysis shown in Figure 1c vs. 1d along with GC/MS analysis (Table 1). In oxidations in H$_2$O, the addition of POM is very beneficial, because the formation of insoluble material is prevented and also the yield of monomers increased by a factor of 2.1. Adding POM to the treatment in MeOH/H$_2$O only increased the amount of monomers by a factor of 1.26 and also the SEC profiles are not very different. It seems that using $H_3PMo_{12}O_{40}$ for obtaining a high yield of monomers is not a necessity if the oxidation is conducted in MeOH/H$_2$O.

Oxidation of two lignosulfonates, one ultrafiltrated sodium lignosulfonate (Ultrazine) and one non-filtrated calcium lignosulfonate (Borresperse), also resulted in a significant reduction of the average molecular weight. Like in oxidations of kraft lignin, the treatment of lignosulfonates in MeOH/H$_2$O leads to compounds with lower molecular weight in comparison to the treatment in H$_2$O. However, no products of higher molecular weight than the untreated lignin were detected in any experiment.

The main reactions of lignin in acidic media have been studied in a variety of investigations (acidolysis, acidic oxygenation, acid sulfite pulping, organosolv pulping, POM delignification). This literature provides a solid basis for the discussion of the underlying chemistry and allows the interpretation of the degradation and polymerization reaction pathways observed by SEC.

Acidolysis (100°C, 0.2 mol l^{-1} HCl in 9:1 dioxane/water) has long been recognized as a method for the characterization of lignins by cleavage of β-O-4 bonds (Lundquist 1992). The reaction route occurring in acidolysis as proposed by Lundquist and Lundgren (1972) is shown in Figure 2. The first step in the cleavage of β-O-4 bonds in lignin units (I, R_1=OAr) is the acid-promoted elimination of a hydroxyl, methoxyl or aroxyl group at the α-carbon leading to a benzyl cation intermediate (II). This step is followed by elimination of the β-proton giving rise to an enol ether, which finally undergoes fast acidic hydrolysis. The formation of benzyl cation intermediates as an initial step is well accepted (Yokoyama and Matsumoto 2008) and common in many treatments of lignin in acidic media. However, treatment of kraft lignin under acidolysis conditions will not bring about a deep-going fragmentation, because most of the aryl-ether bonds have already been cleaved during kraft pulping (Gierer 1980).

A larger variety of lignin interunit linkages are broken when O$_2$ is added to the treatment in acidic media (acidic oxygenation). Gierer and Nilvebrant (1994) studied the reactions of several model compounds that represent structures present in native and in kraft lignins, with O$_2$ in acidic H$_2$O (pH 2.3) at 140°C. All lignin model dimers that can form a
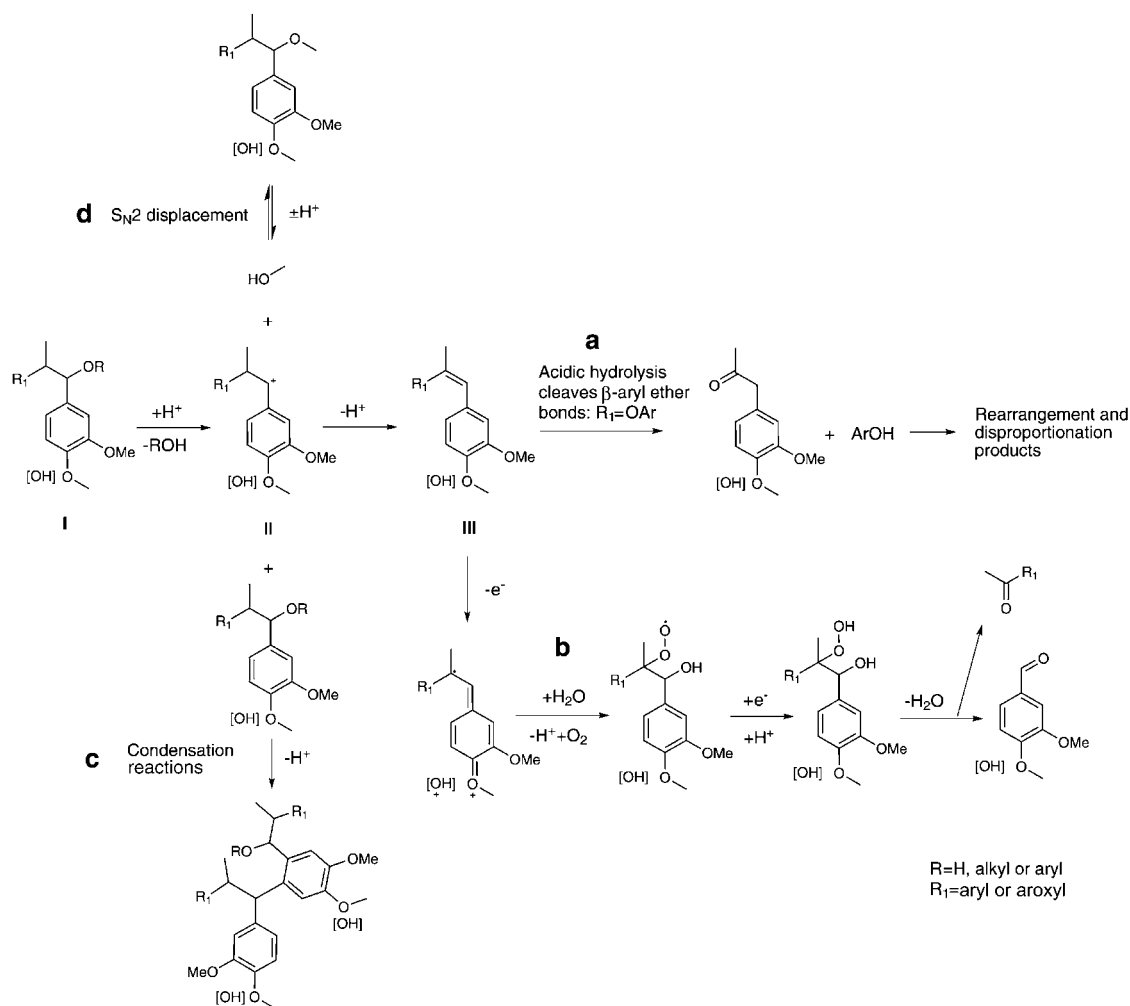
Figure 2 Scheme for reactions of phenolic [OH] and non-phenolic lignin units in acidic media. (a) Acidic hydrolysis (Lundquist and Lundgren 1972); (b) oxidation with oxygen (Gierer and Nilvebrant 1994); (c) condensation reactions (Sarkanen et al. 1971); (d) methanol competes with condensation reactions.

ring-conjugated double bond were at least partially cleaved in the presence of O_2. A reaction mechanism was proposed (Route B in Figure 2) and it was suggested that acidic oxygenation might be employed as an alternative delignification method. Treatment of lignin in acidic media, however, has long been deemed unfeasible, because concurrent condensation reactions result in the formation of higher molecular weight material (Harkin 1966). In the studies by Gierer and Nilvebrant (1994), condensation reactions were mostly prevented by working at very dilute concentrations and an excess of oxygen. This strategy was successful for the oxidation of model dimers, but does not represent an option for the commercial degradation of lignin.

The condensation of lignin in acidic media proceeds via the formation of resonance-stabilized carbonium ions (Route C in Figure 2). Carbonium ions predominately couple with further phenylpropane units at the 5- and 6-position of the electron-rich aromatic ring. Condensation of lignins could be monitored by SEC analysis and results are in agreement with the studies reported in the literature. Condensation of kraft

lignin seems to be the main reaction taking place in the acidic treatment in the absence of oxygen. Addition of oxygen further induced polymerization reactions. Treatment of lignosulfonates consistently did not end up in the formation of a material with higher molecular weight. In acid sulfite pulping, lignin condensation is the second major reaction next to sulfonation. Hence, the lignosulfonates employed in this work have already undergone condensation.

Condensation of lignin is very effectively prevented by addition of MeOH to the acidic media as shown in Figure 1. An explanation for the prevention of condensation reactions with MeOH can also be deduced from the literature. MeOH can react with carbonium ions in a S_N2 displacement resulting in a methoxyl group (Route D in Figure 2), as previously mentioned as a competitive reaction in acidic media by Sarkanen et al. (1971). Provided that the concentration of MeOH is much higher as the concentration of lignin, the condensation with carbonium ion intermediates can be prevented by competitive coupling with MeOH. If the benzyl cation intermediate II is formed from acidic cleavage of a

methoxyl group, the coupling with methanol corresponds to the reverse reaction. The possible prevention of condensation with alcohols has been discussed in a number of publications (Bose et al. 1999; Evtuguin et al. 2000; Oliet et al. 2001), whereas no direct experimental proof has been reported so far.

Conclusion

The combination of POMs as catalysts and methanol as a cosolvent offers manifold new possibilities. With the development and application of a novel SEC method, it was possible to observe acidic condensation of lignin intermediates. These counterproductive polymerization reactions were effectively prevented by addition of MeOH. Having succeeded in the prevention of condensation reactions, one also needs to find a catalyst capable of increasing the yield of monomeric target products. The usage of a commercially available POM, $H_3PMo_{12}O_{40}$, resulted in increased yields of vanillin and methyl vanillate. However, it is unlikely that this particular POM already delivers optimized yields. The screening and development of POMs will certainly be one of the topics of future investigations. In principle, every POM having a redox potential higher than lignin units and lower than O_2 might be used as a redox catalyst. Possible candidates are vanadium containing mixed-addenda anions $[PMo_{12-x}V_xO_{40}]^{(3+x)-}$ which were previously successfully employed in POM delignification (Gaspar et al. 2007).

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