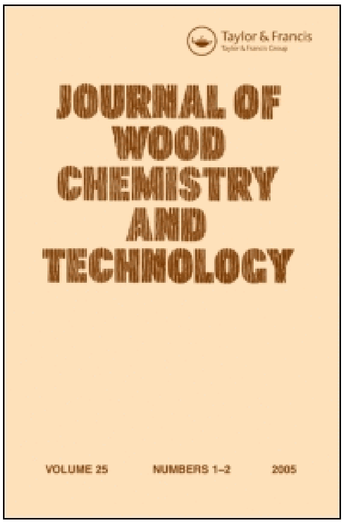

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CONDENSATION REACTIONS OF LIGNIN DURING OXYGEN DELIGNIFICATION UNDER ACIDIC CONDITIONS

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ABSTRACT

Spruce wood (*Picea abies*) has been subjected to delignification by oxygen under acidic conditions using different solvent media. The residual and removed lignins were submitted to permanganate oxidation and the products analyzed by GC and GC-MS. Results from the analysis of the residual lignins indicate that lignin "condensation" depends on the nature of oxidation medium. It was found that the addition of acetone to the aqueous liquor decreases both acid catalyzed and radical side reactions. Lignin "condensation" in water containing media is dominated by radical reactions. Results from the analysis of the lignin removed during oxygen delignification in an acetone/water medium indicate that significant amounts of "condensed" structures are present, which are relatively stable towards oxidation. The presence of diphenylmethane, diarylether and biphenyl type structures in the removed lignin was confirmed by CP-MAS ^{13}C NMR spectroscopy.

INTRODUCTION

Recent progress in the area of oxygen alkaline pulping and bleaching has been a direct result of the extensive studies of lignin oxidation by molecular oxygen over the last 30 years. It is generally agreed that lignin oxidation, with oxygen in alkaline media, is faster than under acidic conditions[1,2]. Little attention has therefore been devoted to the investigation of lignin oxidation in neutral and acidic media. However, it has been shown that all main structural elements, assumed to be present in lignins, are degraded by oxygen in acidic media under relatively mild conditions[3]. It has also been proposed that the decrease of the oxygen delignification rate observed under acidic conditions is a consequence of lignin condensation reactions[4].

Oxygen delignification in acidic media can be accelerated by using mixed aqueous/organic solvent solutions[5]. This has led to the development of the oxygen-organosolv technique[6]. The acidity of the pulping solution is determined by the appearance of organic acids produced via deacetylation of hemicelluloses and oxidation of wood constituents. This procedure can be applied to wood pulping[6-8] or in the valorization of technical lignins [9]. The rate of oxygen delignification in acidic solutions is strongly dependent on the medium composition. For acetone-, acetonitrile-, methanol-, ethanol- and propanol-water media, the rate of delignification has a maximum at 40 % of water (v/v)[6,7]. It has been proposed that the acceleration of delignification with increasing water proportions up to 40 % (v/v) occurs due to the higher solubility of oxidized lignin fragments and to the existence of hydrolytic stages in the process of lignin destruction[10]. The acid catalyzed stages include the transformation of initial lignin units to conjugated structures. Phenylcoumaran and arylglycerol-β-arylether type structures, for example, are converted to stilbene and enol ether types respectively[3,10]. Such conjugated lignin units are oxidized by oxygen much faster than the corresponding lignin structures originally present in the wood tissue. Thus the hydrolytic and homolytic stages during oxygen delignification in acidic media are closely related. In water rich systems (more than 40 %, v/v), it has been proposed that the delignification rate decreases as a consequence of the presence of condensation reactions[10]. These so-called "condensation" reactions (all kinds of reactions competing with lignin destruction) therefore play a significant role in oxygen delignification in acidic media. However, it is not clear what kind of reactions (heterolytic or homolytic) predominate in lignin "condensation" during oxidation with oxygen under acidic conditions and how the nature of the oxidation media influences such reactions. The understanding of the origin and the routes of "condensation" reactions is important from a theoretical point of view and may provide the basis for planning new strategies to improve oxygen delignification in acidic solutions.

This work examines the contribution of the reaction medium to lignin "condensation" during oxygen delignification in acidic aqueous, organic solvent-water (60:40, v/v) and organic solvent media through the analysis of lignins by the permanganate oxidation technique and CP-MAS ^{13}C NMR spectroscopy. Acetone was selected as an aprotic solvent typically used for the oxygen-organosolv delignification.

EXPERIMENTAL

Materials

Spruce wood (*Picea abies*) was used as sawdust (fraction 40-60 mesh) in the delignification studies to eliminate diffusion problems. Standard spruce chips were used for the pulping experiments. The chemical composition (%, o.d.w.) of spruce wood was found to be: Klason lignin - 27.8 %; extractives (diethyl ether) - 1.7 %; holocellulose (peroxyacetic acid method) - 68.5 %. The dioxane lignin with a methoxyl group content of 15.1 % (Zeisel method) was isolated from spruce sawdust according to a published procedure[11]. All solvents used were pro-analysis grade products supplied by Aldrich and Sigma Chem. Comp.

Oxygen Delignification

The oxidation of sawdust in water (WS), acetone (AS) and in an acetone-water (60:40, v/v) solution (AWS) was performed in a PARR reactor (model 4842) with mechanical stirring using the following conditions: liquor-to-wood ratio - 50; initial oxygen pressure - 0.7 MPa; temperature - 150 °C; time-to-temperature - 30 min; time at temperature - 120 min. An experiment in acetone under nitrogen atmosphere (ANS) was run using the same conditions as stated above. After delignification the sawdust was washed with fresh pulping solution then with water and finally dried in the dark at 42 °C. The acidity produced by organic acids formed during the oxidation was determined by potentiometric titration and ranged from 2.2 to 2.8 g/l (equivalent of acetic acid).

The pulping of the chips in the acetone-water 60:40 (v/v) solution was performed in a 2-l shaking reactor using the following conditions: liquor-to wood ratio - 10; initial oxygen pressure - 1.5 MPa; temperature - 150 °C; time to temperature - 20 min; time at temperature - 250 min. The acidity of the spent liquor was 10.5 g/l (equivalent of acetic acid). After cooking, the pulp was washed with fresh pulping solution followed by water and dried at room temperature. The isolation of dissolved lignin from spent liquor was achieved using a previously published method[12]. The yield of pulp was 45.8 % with a Klason lignin content 5.5 %. The yield of the lignin isolated from the pulping liquor was nearly 70 % of the total amount of that removed from wood during delignification. The C9 formula of oxygen-acetone lignin was determined as $C_9O_{4.24}H_{8.14}(OCH_3)_{0.82}$ based on the methoxyl group content data and elemental analysis.

Permanganate Oxidation and Analysis of Products

Potassium permanganate oxidation (PO) was performed with 50 mg of lignin or with a corresponding amount of sawdust or pulp (calculated as lignin)[13]. Methylated oxidation products were analyzed by gas chromatography

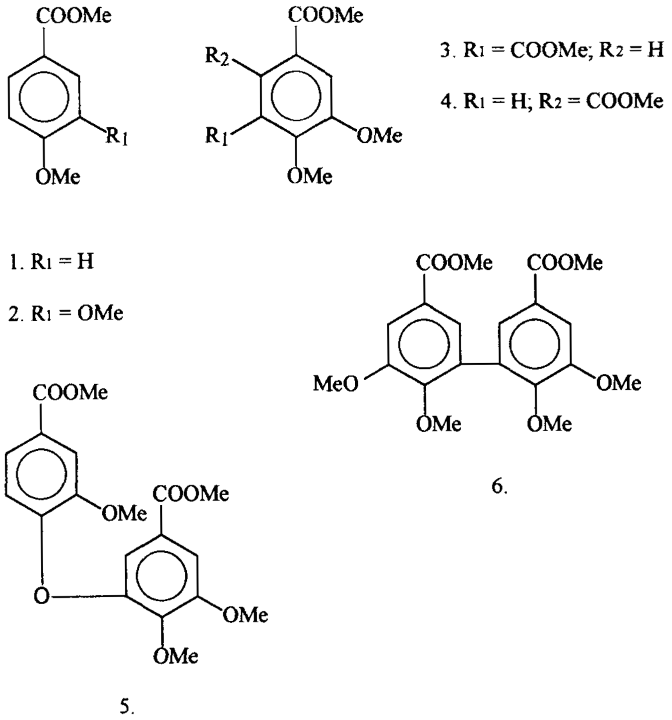

FIGURE 1. Permanganate Oxidation Products of Spruce lignins.

on a Varian Star 3400CX chromatograph equipped with fused silica capillary column SPB-5 (30 m x 0.25 mm i.d.; 25 mm film thickness; Supelco). The chromatographic conditions were as follows: initial temperature - 150°C; temperature rate - 5 °C/min; final temperature - 260 °C; injector temperature - 220°C; FID temperature - 270 °C. More than 95 % of oxidation products were identified and quantified. All individual esters were identified based on their retention times and mass spectra using a VG Autospec-Q spectrometer. The quantification of permanganate oxidation products **1-6** (FIGURE 1) was performed using pyromellitic acid tetramethyl ester as internal standard[14].

CP-MAS ^{13}C NMR Spectroscopy

^{13}C solid state NMR spectra were recorded at 100.6 MHz (9.4 T) on a Bruker MSL-400 spectrometer. A 7-mm double bearing Bruker rotor was spun in air at 5.0 kHz. In all experiments the ^{1}H and ^{13}C 90° pulses were ca. 4 μs. The CP-MAS spectra were recorded with a 3 s recycle delay and a 1.5 ms contact time.

RESULTS AND DISCUSSION

Permanganate Oxidation of Treated Sawdust

Permanganate oxidation (PO) is a suitable technique for the study of condensed structures of both isolated and residual lignins[13,14]. Although only the phenolic phenylpropane units are accessible to this analysis (25-35 % of total units), it is assumed that they reflect the structural tendencies of the lignin as a whole[15]. Taking into account that phenolic units are the most reactive in lignin both under oxidation with oxygen and acidolysis, their analysis provides important information concerning the routes in lignin "condensation" reactions during oxygen-organosolv pulping.

The results of oxygen delignification of spruce sawdust in different media are shown in TABLE 1. The six most prominent degradation acids obtained after the PO of the pulping residue are presented in FIGURE 1. TABLE 2 represents the frequency of occurrence of PO products of residual lignin in sawdust after delignification in acetone, acetone-water 60 : 40 (v/v) and aqueous solutions .

The changes in the distribution of different PO products from lignin in residue after the pulping compared to wood provides information about the priorities of the "condensation" of lignin during delignification. Thus the presence of isohemipinic acid dimethyl ester **3** and *m*-hemipinic acid dimethyl ester **4** indicate the occurrence of acid catalyzed condensation reactions with participation of the benzylic cation in position five and six, respectively, of the

TABLE 1

Results of the Oxygen Delignification of Spruce Sawdust.

Oxidation medium	Sample	Yield of residual solids, % (w/w)	Lignin in residual solids, %, (w/w)
Acetone	AS	95.3	26.6
Acetone/water, 60/40 (v/v)	AWS	71.4	21.0
Water	WS	66.5	29.0
Acetone (under N_2)	ANS	96.5	27.4

TABLE 2

Frequency of Occurrence of PO Products of Residual Lignin in Treated Sawdust.

Sample	Frequency of carboxylic acids (analyzed as methyl esters), mol %						Yield of esters, %, w/w (/Klason lignin)
	1	**2**	**3**	**4**	**5**	**6**	
Initial sawdust	4	71	10	6	3	6	14.7
AS	3	63	10	11	5	8	13.1
AWS	4	58	12	8	6	12	15.6
WS	2	48	17	8	8	17	17.2
ANS	3	66	11	10	3	7	12.7

(key to designations for samples in TABLE 1 and PO products in FIGURE 1) guaiacyl lignin units. The presence of dimeric structures of types **5** and **6** can be considered to be a result of radical recombination reactions of phenoxyl radical mesomeric forms. The appearance of these products (**5** and **6**) depends on the presence of pressurized oxygen in the pulping atmosphere. The treatment of sawdust in a nitrogen atmosphere (sample ANS, TABLE 2) showed practically the same level of dimeric structures of type **5** and **6** as in initial wood, while the treatment of sawdust in the presence of oxygen (sample AS) yielded higher amounts of these structures. Radical coupling has already been proposed as one of the routes for lignin "condensation" during oxygen-organosolv pulping. This is supported by the results of ^{13}C NMR studies of oxygen-acetone spruce lignins isolated from pulping liquor[16]. Results obtained using lignin model compounds also indicated that the recombination of phenolic radical mesomeric forms is the main source of condensed products under oxygen oxidation in weak alkaline media[17].

The proportions of the PO products **1-6** are highly dependent on the delignification medium. The PO products of residual lignin in sawdust, obtained after oxygen delignification in an acetone medium (sample AS, TABLE 2), show a 9 % increase in "condensed" structures (increasing the frequency of occurrence of **3-6** based on the level in untreated sawdust) compared to 13 % and 25 % after the sawdust processing in acetone-water (sample AWS) and aqueous (sample WS) solutions respectively. These results confirm the increase of lignin "condensation" during oxidation in water rich solutions. These observations can not be the consequence of a simple accumulation of cross-linked structures in wood tissue since the degree of delignification is low, especially in acetone and aqueous solutions.

Several conclusions can be drawn concerning lignin "condensation" during oxygen delignification in acidic media. Oxygen delignification in an acetone medium is followed by the appearance in residual lignin of approximately equal amounts of "condensed" structures, caused by acid catalyzed and radical reactions, relative to untreated wood (increasing the frequency of occurrence of products **3, 4** and **5, 6** in sample AS). In contrast, for water containing media, the contribution of radical reactions to the condensation was increased. When oxidation was carried out in water or in acetone-water solution (samples AW and AWS, respectively) the amount of products **5** and **6** obtained during PO, was double that for products **3** and **4**. The increase in the total amount of ”condensed” structures **3-6** in residual lignin, after delignification in acetone-water solution, was half that observed in water (based on the level in untreated sawdust).

A possible explanation for the increasing role of radical reactions in lignin condensation in water containing media is the phenomena of solvent "cage" action. Solvents such as water, which have the ability to participate in hydrogen bonding, form a "cage" around radical species in solution. This "cage" stabilizes the radicals against disproportionation reactions, due to an electron-donor effect and suppresses propagation chain reactions due to an isolation effect[18]. At the same time, the contribution of recombination reactions is increased. This effect explains, for example, the suppression of free radical chain reactions for several organic compounds during oxygen oxidation in the presence of water[18]. Therefore, this solvent "cage" effect in the presence of water can explain the increasing lignin ”condensation” by radical recombination reactions of phenoxyl radical mesomeric forms. Increasing the acetone percentage in the acetone-water oxidation medium may lead to the loosening of the solvent "cage" through the disturbance of the regular hydrogen-bonded structure of water. This could explain the decrease in the relative amounts of PO products **5** and **6** from sawdust after delignification in acetone-water medium when compared to oxygen delignification in water.

Another explanation for the dependence of lignin radical coupling on the composition of pulping media can be envisaged. Although the acetone itself, without the wood material, is stable towards oxidation with molecular oxygen under pulping conditions, it is evident that the different radical oxygen species that appear during lignin autooxidation (such as hydroxy and hydroperoxy radicals) can participate in reactions with acetone. In the latter case, acetone can form relatively stable peroxides and therefore play a role as an inhibitor of radical chain reactions. Thus, the presence of acetone in pulping solutions can decrease the extent of lignin radical coupling reactions through a ”termination” effect. Apparently, this effect is not so important under the delignification conditions used. The peroxides concentrations found in pulping solutions (iodometric determination) under the conditions of sawdust delignification are quite low and the change is insignificant on going from an acetone (16.4 mg active oxygen/l) to acetone-water (60:40,v/v) medium (13.7 mg active oxygen/l).

The reduction of acid catalyzed condensation reactions in the presence of acetone followed by the decreasing of PO products **3** and **4** can be explained by the poor dissociation of organic acids in a pulping solution containing an organic solvent.

Permanganate Oxidation of the Residual Lignin in Pulp and in Pulping Liquor

Oxygen delignification of chips compared with sawdust is complicated by diffusion problems. In addition, chips pulping occurs at low liquor-to-wood ratios which favors lignin "condensation" reactions in bulk and in solution. It is interesting to compare the abundance and proportions of different "condensed" structures in residual and removed lignins at a high degree of chips delignification when structural changes, appearing due to competing lignin reactions, should be significant.

The results presented in TABLE 3 show the difference in frequency of occurrence of different kinds of "condensed" structures based on PO products of the residual lignin in oxygen-acetone spruce pulp and of the lignin isolated from spent liquor. The residual lignin in pulp shows a higher level of "condensation" than in sawdust delignified to lower degree (sample AWS, TABLE 2), although the relative proportions of "condensed" structures appearing after the delignification are very similar. Compared with the data for the residual lignin, the lignin in pulping liquor gives, after PO, a higher amount of product **3** indicating the occurrence of "condensation" reactions in position five of lignin guaiacyl units. The likely structures that can produce **3** are α-5 type structures that appear in lignin as the result of the well known acid catalyzed condensation reactions with participation of a benzylic cation. The formation of "condensed structures by radical coupling reactions giving product **3**, can also not be excluded. The high amount of **3** after PO of dissolved lignin is, at least partially, a consequence of lignin secondary reactions

TABLE 3

Frequency of Occurrence of PO Products of Residual Lignin in Oxygen-Acetone Pulp and of Lignin Isolated from the Pulping Liquor.

Sample	Frequency of carboxylic acids (analyzed as methyl esters), mol %						Yield of esters, %, w/w (/Klason lignin)
	1	**2**	**3**	**4**	**5**	**6**	
Residual lignin in pulp	3	49	14	11	9	14	11.2
Lignin isolated from the pulping liquor	2	41	31	6	6	14	16.7

(key to designations in FIGURE 1)

in the pulping solution. Lignin structural units bonded by α-5 linkages are resistant towards acidolysis and oxidation with oxygen. Hence, their level in lignin fragments dissolved in pulping liquor during the oxygen delignification can increase, giving a high yield of isohemipinic acid after the PO procedure.

CP-MAS ^{13}C NMR Analysis of Lignin Isolated from the Pulping Liquor

The CP-MAS ^{13}C NMR spectrum of lignin isolated from the pulping liquor (FIGURE 2, B) indicates a carbon resonance at around 29.7 ppm. This resonance is not clearly present in the spectrum of spruce dioxane lignin (FIGURE 2, A) which is used as a reference for natural lignin in wood. As the differences in chemical shifts for lignin in the solid state and in solution ^{13}C NMR spectra are in most cases insignificant[19], the signal assignments found in solutions can be applied to the solid state results. From ^{13}C NMR of lignins in solution[20], the resonance at 29.7 ppm can be attributed to the methylene carbon in diphenylmethane (DPM) structures (FIGURE 3). DPM structures

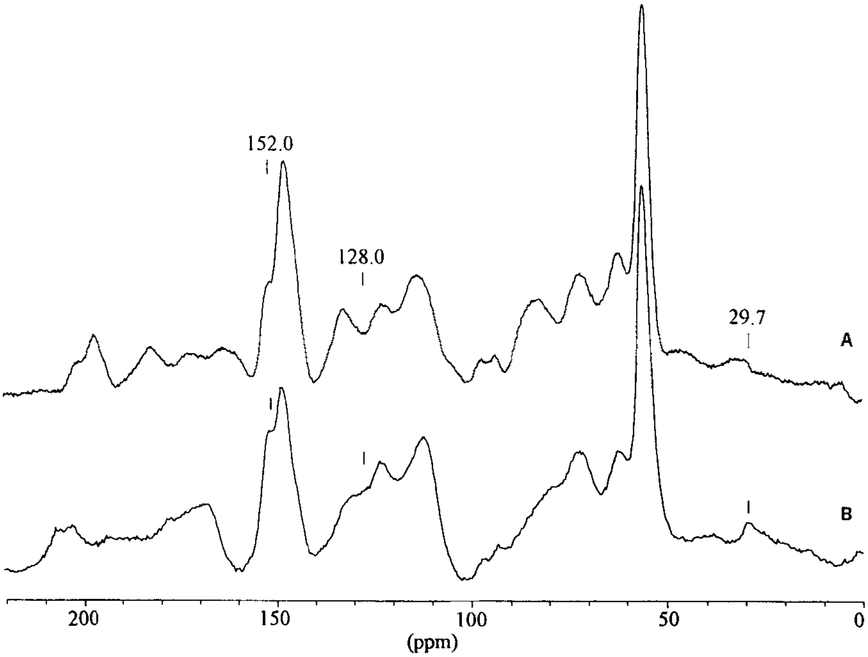

FIGURE 2. CP-MAS ^{13}C NMR Spectra of Spruce Dioxane Lignin (A) and Lignin Isolated from Oxygen-Acetone Pulping Liquor (B).

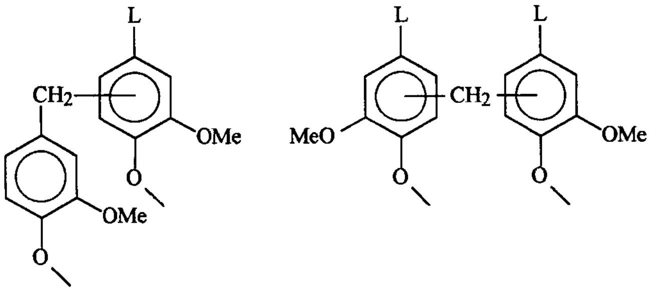

FIGURE 3. Proposed Diphenylmethane (DPM) Type Structures in Lignin Isolated From Oxygen-Acetone Pulping Liquor.

together with α-5, diarylether and biphenyl type structures are relatively stable under oxygen oxidation conditions[15,21] and could accumulate in lignin macromolecules dissolved in pulping liquor during oxygen delignification. This probably explains the reported relative stability of oxygen-organosolv lignins in pulping solutions[6-8,12].

According to published results on lignins analyzed by solid state CP-MAS ^{13}C NMR spectroscopy, the appearance of a resonance at 128.0 ppm can indicate that significant amounts of C-5 substituted guaiacyl units are present[22]. The results obtained from the analysis of PO products (TABLE 3) and CP-MAS ^{13}C NMR (FIGURE 2, B) of isolated lignin support this. The CP-MAS ^{13}C NMR spectrum of lignin isolated from the pulping liquor also confirms the presence of large amounts of 5-5′ and 4-O-5 dimeric structures. This is based on the appearance of a strong resonance at 152.0 ppm, previously assigned using lignin model compounds to C-5/C-5' and C-5 aromatic carbons in former structures[23].

CONCLUSIONS

The results obtained for permanganate oxidation of residual and isolated lignins from oxygen delignification of wood under acidic conditions clearly indicate that lignin "condensation" depends on the nature of the oxidation medium. The addition of acetone to the aqueous liquor decreases both acid catalyzed and radical reactions, favoring an increase in the overall rate of delignification. In oxygen delignification in acidic media, lignin "condensation" is mainly a result of radical reactions. Results from the analysis of lignin removed during oxygen delignification of chips in acetone/water medium indicate that significant amounts of "condensed" structures, which are relatively stable towards oxidation in acidic media, are present. The presence of diphenylmethane, diarylether and biphenyl type structures was confirmed by CP-MAS ^{13}C NMR spectroscopy.

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