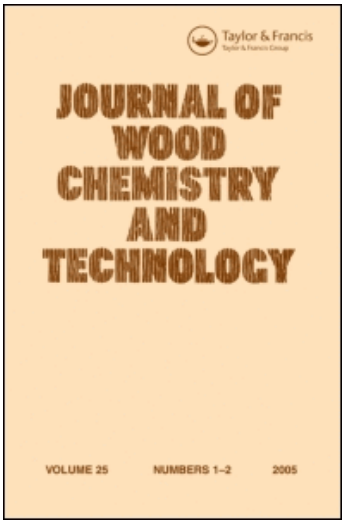

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STRUCTURE AND REACTIVITY OF SPRUCE MECHANICAL PULP LIGNINS PART II. ORGANOSOLV FRACTIONATION OF LIGNINS IN A FLOW-THROUGH REACTOR

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ABSTRACT

Various spruce mechanical pulps were subjected to delignification with ethanol-water (1 : 1, v / v) containing 0.1 M acetic acid at 175 °C in a flow-through reactor. A thermomechanical pulp (TMP) and the corresponding samples derived from its bleaching (BTMP) and yellowing (YBTMP) treatments were delignified to a similar extent, about 70 % of delignification degree, as compared with spruce wood. A series of five successive lignin fractions was recovered from each pulp sample and then characterized by various analytical methods. Large structural variations were observed within these fractions. The number of phenolic structures appeared to be an important factor influencing the dissolution of lignins in the ethanol-water medium. These lignin fractions were found to be different in the amount of β-aryl ether structures and in the relative importance of main carbon-carbon bonding patterns. The results are discussed in relation to the lignin fractionation in the flow-through reactor.

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INTRODUCTION

In the first part of this series,[1] structural changes of *in situ* spruce TMP lignins during bleaching and photoyellowing were reported. In order to gain more detailed information about the behaviour of lignin in these processes, our investigations were extended to lignins isolated from the TMP sample and the corresponding bleached (BTMP) and photoyellowed (YBTMP) ones.

Owing to the structural complexity and heterogeneity of lignin, none of the usual isolation procedures satisfies the needed representativity not only in term of yield but in term of structural integrity as well.[2] Lignins isolated by means of chemical modifications have been used in the field of fundamental studies of lignin because of procedure simplicity and of high yield. In this case, the following reactions take place:

- primary degradation leading to depolymerization of *in situ* lignin and breakdown of lignin polysaccharide associations;

- secondary reactions leading to repolymerization of certain fragments and / or hydrolysis of dissolved macromolecules.

In order to reduce the occurrence of secondary reactions, it was proposed to remove the dissolved lignins from the site of reaction as quickly as possible and to cool the extraction solution immediately. For this purpose several apparatuses have been reported in the literature.[3 - 5] The most widely used is the flow-through reactor.[6 - 8] It was demonstrated that the flow-through mode allowed both higher delignification rate and better selectivity, as compared with the batch one.[9] Consequently, the recovered lignins are likely to possess more original structural features because of reduced secondary reactions.

On the other hand, organosolv delignification has been developed as a potential approach not only as an alternative to conventional pulping but also for total biomass utilization. Furthermore, organosolv lignins have been used for structural investigations of lignin because they are readily isolated in high yield and without severe chemical modification.[10] Among a large number of solvents, aqueous ethanol is one of the most promising since it is easily recovered at low cost.[11] During organosolv delignification, lignins are dissolved essentially by acid-catalyzed cleavage of such bonds as α-aryl ether and arylglycerol-β-aryl ether of lignin macromolecules.[12] In the case of softwood it was found necessary to add a

small amount of catalysts such as mineral acids to accelerate the solvolysis of lignin.

In the present paper, we describe the application of such a flow-through reactor to the fractional isolation of lignin from various spruce TMP samples using ethanol-water (1 : 1 v/v) containing 0.1 M acetic acid. The lignins isolated from each pulp sample were recovered in five successive fractions. The structural variations in these lignin fractions were observed with respect to elemental composition, functional group content and main interunit linkages.

Thioacidolysis allowed an estimate of the amount of non-condensed β-aryl ether structures from the determination of the main recovered monomeric products.[13] However, carbon-carbon bonds and some other diaryl ether structures are not cleaved upon thioacidolysis and are referred to as condensed. A two-step degradative method, thioacidolysis followed by Raney nickel desulfuration, was developed to estimate the amount of these structures through the determination of main dimeric degradation products in the thioacidolysis mixture.[14] These dimers originate from the so called 5-5, β-5, β-1, 4-O-5 and THF ring interunit linkages, as outlined in the preceding paper of this series.[1]

Finally, in order to check the chemical modifications accompanying the organosolv fractionation, a re-cooking experiment was designed in which an isolated lignin fraction was treated with the same solvent as used in the organosolv fractionation. A lignin fraction isolated at the beginning of delignification process was used for this batch cooking treatment.

RESULTS AND DISCUSSION

1. Delignification Aspect

The extent of delignification is given in Table 1 for each sample (wood or pulp) used in this work. It can be seen that there was only a small difference between wood and TMP. This suggests that no substantial modification took place in lignin during the thermomechanical process.

TABLE 1. Delignification Data

Starting material	Residual pulp yield (%)	Initial lignin content (%) *	Final lignin content (%) *	Degree of delignification (%)
Wood	55.0	28.5	16.6	68.0
TMP	53.8	29.0	15.3	72.0
BTMP	61.8	28.4	14.2	69.1
YBTMP-1	62.5	26.2	14.1	66.4
CTMP	50.5	27.7	5.8	89.8

*: as Klason lignin

In addition, the degree of delignification of CTMP sample was considerably higher than that of wood or TMP, indicating that the CTMP lignin can be extracted by aqueous ethanol in larger amounts. It is reasonable to assume that the sulfonic acid groups which were introduced during sulfonation improved the dissolution of lignin in the organosolv medium. On the other hand, this chemical pretreatment might also increase the accessibility to the delignifying agent since it increased the specific surfaces and hydrophilicity of fibers.[15]

Neither bleaching nor photoyellowing seemed to induce significant changes in extractability of lignin. However, the yields of residual pulp for BTMP and YBTMP-1 were considerably higher than that for the original TMP. Reasons for this are not well understood. One possible explanation is that some easily soluble components of TMP, such as lignin and hemicellulose fragments, were already removed with the bleaching liquor before the organosolv treatment.

2. Material Balance and Lignin Recovery

A preliminary experiment was conducted to evaluate the variation in the concentration of extracted lignins in the course of delignification. The solution issued from the reactor was collected in numerous tubes. After appropriate dilution,

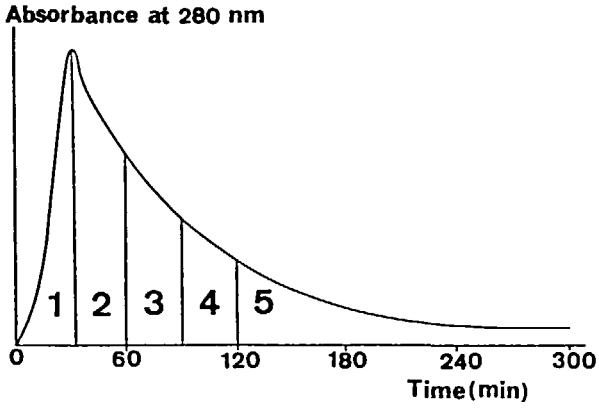

FIGURE 1. UV absorbance of the solution issued from the flow-through reactor as a function of delignification time (Starting material: TMP).

TABLE 2. Material Balance of Recovered Components

Recovery, as % of starting material	Sample				
	Wood	TMP	BTMP	YBTMP-1	CTMP
Residual pulp	55.0	53.8	61.8	62.5	50.5
Water-precipitable portion	14.1	13.6	12.7	13.1	6.8
Water-soluble portion	32.5	34.8	29.3	26.7	41.3
Total recovery	101.6	102.2	103.8	102.3	98.6

the UV absorbance of solution in each tube was measured at 280 nm. Figure 1 gives an example of an elution curve. Absorbance rose sharply to a maximum at the very beginning of delignification, and then decreased gradually. The five lignin fractions which were recovered in this study corresponded to the five zones indicated in this figure.

Material balance of recovered components is reported in Table 2 for each experiment. Recovery was close to 100 %.

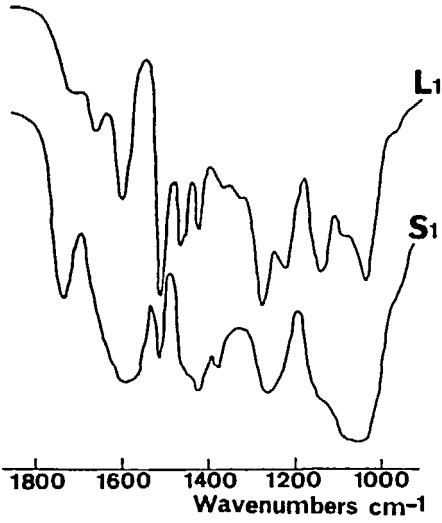

FIGURE 2. Infrared spectra of water-precipitable (L_1) and water-soluble (S_1) fractions isolated from TMP.

The precipitated fractions (L_1 - L_5) were essentially composed of lignin, whereas the corresponding water-soluble fractions (S_1 - S_5) contained water-soluble lignins and dissolved carbohydrates. This is clearly shown by comparison of the IR spectra of these two categories of fractions. Figure 2 gives the IR spectra of L_1 and S_1 fractions. Similar results were observed for the other fractions. It appeared that the water-soluble fractions had a very low content of lignin. The characteristic IR absorption bands of lignin, at 1600, 1510 and 1465 cm^{-1}, were largely masked by those of polysaccharides.

Table 3 shows the relative weight percentages of the five precipitated lignin fractions (L_1 - L_5) as well as their cumulative yield for each tested sample. It can be seen that the relative proportions of the various fractions are similar within all these samples except CTMP. The first fractions, released at the beginning of the cook, were of low yield and should be composed of easily extracted lignin fragments; they also were likely to contain nonlignin components other than polysaccharides.[16]

TABLE 3. Relative Weight Percentages (%) of Five Successive Lignin Fractions Recovered, as Water-Precipitable, from Organosolv Delignification Effluents.

	Wood	TMP	BTMP	YBTMP-1	CTMP
L_1 (0 - 30 min)	9.5	6.0	5.7	6.1	19.2
L_2 (30 - 60 min)	21.8	21.2	22.6	20.2	52.6
L_3 (60 -90 min)	19.4	21.2	19.0	14.9	12.6
L_4 (90 - 120 min)	18.1	16.0	13.6	13.3	2.9
L_5 (120 - 300 min)	31.2	35.6	39.0	45.5	12.6
Total (1)	71.4	65.0	65.7	74.8	27.4
(2)	48.6	46.8	44.6	49.7	24.6

(1) and (2): Percentages of total recovered lignins (L_1 - L_5) on the basis of the total extracted lignins and the lignins present in the starting materials, respectively.

TABLE 4. Sulphur Content (%) of Different Lignin Fractions from CTMP.

Fraction No	Precipitable portion (L)	Soluble portion (S) *
1	0.54	2.06
2	0.54	1.28
3	0.52	1.00

* : Corrected for sugar content

In contrast, the data for CTMP appeared to be different. The first two fractions, particularly L_2, were the most abundant parts of the water-precipitable lignins. It is confirmed that the CTMP lignins were easily solubilized in the organosolv medium. This is in agreement with the large extent of delignification observed for that pulp sample. Moreover, the low quantity of the last two fractions L_4 and L_5 could be due to the fact that at a high degree of delignification the lignin fragments are closely associated with polysaccharides and thus tend to remain in the water phase.

As shown in Table 3, the majority of the extracted lignins from wood, TMP, BTMP or YBTMP-1 sample could be recovered as water-precipitable lignin, whereas in the case of CTMP the precipitated lignins merely represented a small part of the total dissolved lignins. As discussed above, it is likely that the sulfonic acid groups made the CTMP lignins more soluble in water. This assumption is strongly supported by the difference in sulphur content between the two parts of lignin, i.e. precipitable and soluble (Table 4).

It should be noted that the lignins L_1 - L_5 obtained from the TMP, BTMP and YBTMP-1 samples represented about 50 % of the lignins present in the starting materials. In the present work, therefore, these lignin fractions were used as substrates for structural characterization of lignin.

3. Characterization of Lignin Fractions

The main purpose of this work was to study structural differences of lignins isolated by the organosolv fractionation in the flow-through reactor. For the sake of brevity and clarity, accordingly, we only report on the series of lignin fractions isolated from the TMP sample. Similar variations were observed for the other series of lignins isolated from the BTMP and YBTMP-1 samples.

The elemental composition and empirical C_9 formula of the five lignin fractions extracted from the TMP sample are given in Table 5.

The first fraction L_1 exhibited a high content of carbon and a low content of oxygen. This could be considered as an indication of the presence of nonlignin substances other than sugars in this sample. The presence of nonlignin portions which are likely extractives was previously reported by Lindner and Wegener [16] in their organosolv lignin samples. This is further supported by the variation in the content of methoxyl group. Since at the beginning of delignification a noticeable cleavage of methoxyl group seems impossible, the low methoxyl value obtained for L_1 should be attributed to the aforementioned impurities.

The other lignin fractions (L_2 - L_5) presented a similar elemental composition. Their contents of carbon, hydrogen, oxygen and methoxyl were close to those reported in the literature for spruce MWL.[17] However, the " normal " ethanol-water lignins, i.e. obtained from batch ethanol-water cooking, are of higher carbon content and lower oxygen content,[18 - 20] indicating that these lignins

TABLE 5. Elemental Composition, Methoxyl and Ethoxyl Contents and C_9 Formula of TMP Lignin Fractions L_1 - L_5 (Values are corrected for sugars).

	C (%)	H (%)	O (%)	OCH_3 (%)	OC_2H_5 (%)	C_9 formula
L_1	65.50	6.37	28.13	14.46	2.21	$C_9H_{8.67}O_{2.28}(OCH_3)_{0.86}(OC_2H_5)_{0.09}$
L_2	63.40	6.43	30.18	15.70	3.66	$C_9H_{8.78}O_{2.54}(OCH_3)_{0.99}(OC_2H_5)_{0.16}$
L_3	63.24	6.18	30.58	14.87	3.66	$C_9H_{8.44}O_{2.62}(OCH_3)_{0.93}(OC_2H_5)_{0.16}$
L_4	63.76	6.23	30.01	15.50	3.56	$C_9H_{8.38}O_{2.52}(OCH_3)_{0.97}(OC_2H_5)_{0.15}$
L_5	64.14	6.26	29.60	15.23	3.85	$C_9H_{8.35}O_{2.44}(OCH_3)_{0.94}(OC_2H_5)_{0.17}$

undergo condensation to a noticeable extent. It can therefore be concluded that the extent to which lignins isolated by the flow-through manner suffer secondary reactions is less significant.

It is interesting to note that all fractions contained a certain number of ethoxyl groups, which is a typical characteristic of ethanol-water lignins.[18 - 20] The introduction of ethoxyl groups indicates that ethylation of lignin took place during the organosolv delignification. According to previous results,[12, 21, 22] acid-catalyzed alkylation of lignin, which always accompanies the alcohol cooking, occurs mainly at the α position of the side chain. This reaction should reasonably lead to a reduced content of alcoholic hydroxyl groups, which will be discussed later.

Thioacidolysis was used to gain more detailed information about the lignin structure. As illustrated in Figure 3, it is possible to distinguish between non-condensed β-aryl ether linked guaiacyl units located as end groups of the lignin polymer chain and the analogues located in the interior of the chain, when the phenolic hydroxyl groups of lignin are methylated prior to thioacidolysis. Therefore, the A / (A + B) ratio should directly reflect the frequency of free phenolic hydroxyl groups in the β-aryl ether linked guaiacyl structures.[23]

The results obtained for the TMP sample, lignin fractions and residual pulp are shown in Table 6. As previously reported,[1] there was no difference in the content of non-condensed β-aryl ether structure between spruce wood and TMP

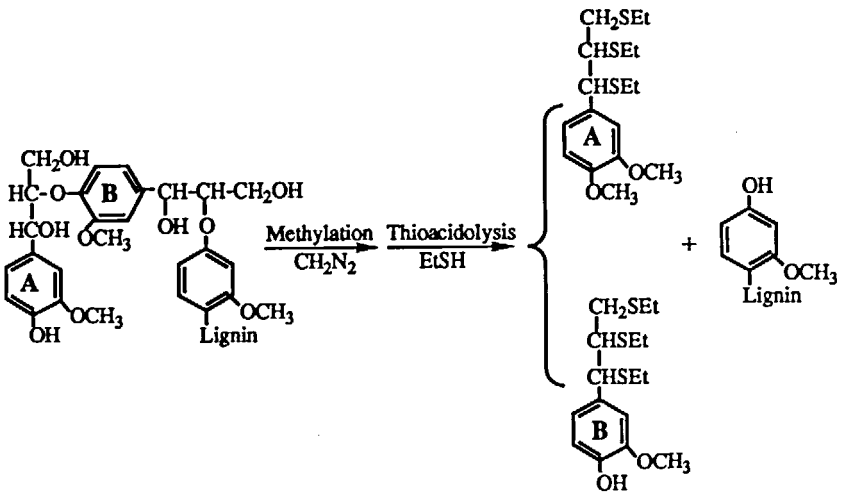

FIGURE 3. Scheme of thioacidolysis of CH_2N_2-methylated lignins: main recovered monomers issued from non-condensed β-aryl ether structures in terminal units (A) and internal units (B) of the lignin polymer chain.

TABLE 6. Amount of Non-Condensed β-Aryl Ether Linked Guaiacyl Structures (A + B) and Frequency of Their Phenolic Moiety (A) of TMP, Isolated Lignins from TMP and Residual Pulp.

Sample	(A + B) μmol / g lignin	% A / (A + B)
TMP	1160	21.9
L1	840	31.4
L2	803	25.0
L3	808	19.7
L4	763	16.2
L5	624	12.4
Residual pulp	420	6.9

lignins. On the other hand, the amounts of this structure in the lignin fractions were close to that of spruce MWL sample,[14] except for L_5 which was isolated at the later stage of the organosolv delignification and appeared to be more condensed.

It was observed that the number of non-condensed β-aryl ether structures decreased as the organosolv cook proceeded. It is thought that a certain cleavage of this linkage took place during this process. This may be characteristic of softwood organosolv delignification, as compared with the case of hardwood in which α-aryl ether bond cleavage plays a dominant part.[10] However, it can be seen that at the end of delignification the residual lignin still contained a rather appreciable amount of β-aryl ether structure. The quite low efficiency of β-O-4 cleavage showed again that aqueous ethanol, contrary to what was observed during kraft cooking,[24] does not modify the lignin to a large extent.

It is interesting to note that the proportion of free phenolic β-aryl ether structures (A) drastically declined with increasing duration of delignification. At the end of delignification, the residual lignins no longer contained sufficient free phenolic hydroxyl groups so that considerable amounts of residual lignins could not be further removed by extended cooking under the conditions used here. Thus, it is reasonable to assume that a minimum amount of phenolic structures is a necessary prerequisite for making lignin fragments soluble in the solvent. This observation will be further confirmed by estimating the total phenolic hydroxyl content.

As shown in Table 6, the first fraction (L_1) had a highest content of free phenolic hydroxyl group. The average value of phenolic units for the whole series of fractions, calculated on the basis of weight proportion of each fraction, was equal to 18.7 %, i.e. lower than that of the TMP *in situ* lignin. This discrepancy may be due to the fact that the water-soluble lignin portion is richer in free phenolic units (for example 37.5 % of A / (A + B) for S_1).

The total yield of the various dimers and their relative proportion are given in Table 7. It can be observed that the total amount of these dimers represented about 30 % (molar percentage) of the main recovered thioacidolysis monomers in all the lignin samples, either *in situ* or isolated, which is in accordance with previous results.[14] Similarly to the case of *in situ* lignins,[1] the main condensed linkage patterns are β-5, β-1 and 5-5 in the spruce isolated lignins.

The relative importances of the various condensed bonds obtained for the isolated TMP lignins were fairly different from those obtained for the *in situ*

TABLE 7. Total Yield and Relative Molar Percentage of Main Dimeric Products Obtained from Thioacidolysis of TMP, Isolated Lignins and Residual Pulp.

Sample	Total yield (%*)	Relative molar percentage (%)				
		5-5	β-5	β-1	4-O-5	THF**
TMP	31	29.5	34.1	25.6	7.7	3.1
L_1	34	21.2	29.9	37.8	5.3	5.7
L_2	34	21.2	34.4	33.4	4.9	5.9
L_3	34	22.2	40.6	26.1	5.7	5.4
L_4	30	21.8	43.6	22.7	7.0	4.8
L_5	26	22.1	48.9	18.0	7.3	3.5
Residual pulp	30	23.2	46.9	13.6	16.2	n.d.

*: molar percentage on the basis of the main recovered monomers issued from non condensed β-O-4 linked guaiacyl structures (in Table 6)

**: β-β type dimer: D,L-3,4-divanillyltetrahydrofuran
n.d. : not determined

TABLE 8. Thioacidolysis Products of TMP L_2 Fraction Before and After Re-cooking.

	Before re-cooking	After re-cooking
β-O-4 linked guaiacyl units (μmol / g lignin)	803	397
Total yield of dimers (μmol / g lignin)	287	134
Relative molar percentages (%) of various dimeric products		
5-5	21.2	15.5
β-5	34.4	48.6
β-1	33.4	23.0
4-O-5	4.9	6.9
THF**	5.9	6.0

**: as in Table 7

lignins. This can be assigned to the lignin heterogeneity revealed by the organosolv fractionation and / or to the effect of cooking in the reactor. Further experiments will be carried out to clarify this point.

From the data of Table 7, it can be clearly seen that the β-1 structures were quite abundant in the lignin isolated at the beginning of delignification process and that their relative importance significantly decreased in the course of the cooking process. In addition, the corresponding water-soluble lignin fractions (S_1 - S_5) were found to be much richer in these structures.[25] In agreement with previous results,[26] it can be concluded that the β-1 diarylpropane structures are more closely associated with easily solubilized lignin fragments. This conclusion is in accordance with a recent report indicating that the β-1 structures were present mainly as phenolic end groups and were rapidly liberated from the lignin macromolecule under acidic conditions.[27]

Inversely, there was a concomitant increase in the amount of β-5 structures in the isolated lignins. It is likely that the β-5 linkages, occurring primarily in the phenylcoumaran structure,[28] were too stable to be broken down by the organosolv treatment. On the other hand, another possible explanation is that some β-5 structures were formed during the organosolv cooking. As proposed by Sarkanen,[12] phenolic β-aryl ether structures may undergo homolytic cleavage and convert to rearranged phenylcoumaran structures under acidic organosolv conditions.

Besides, the proportion of 5-5 biphenyl bonding pattern appeared to remain constant in all the lignin fractions.

The 4-O-5 diaryl ether structure was found to be of higher frequency in the lignin isolated at the later stage of delignification and in the residual lignins as well. This observation indicates that this structure was resistant to the organosolv treatment. However, it cannot be excluded that some 4-O-5 bonds were formed during the cooking process.

Finally the THF ring type structure was only minor. Its amount decreased from L_1 to L_5.

The results discussed above have shown that apparent differences within the five lignin fractions were revealed by the fractionation owing to the lignin heterogeneity. Whether or not the organosolv treatment itself affected the structure of isolated lignins was checked by submitting the isolated sample L_2 to a re-cooking process. Analysis of monomeric and dimeric products recovered from the thioacidolysis of this re-cooked L_2 sample was carried out and compared with that of the original L_2 sample (Table 8).

It can be seen that the amount of non-condensed β-aryl ether structure after re-cooking was half as much as before the treatment. This decrease can be attributed to condensation reactions which are likely to occur under the treatment conditions used here. On the other hand, the yield of dimers was reduced to a similar extent. This result suggests that the re-cooked lignin sample suffered condensation and was highly cross-linked.

From the data of Table 8, it is worth noting that the re-cooking treatment led to an increase in the relative importance of β-5 structures and a simultaneous decrease in that of β-1 structures. This observation is in agreement with the results obtained in the previous section. Roughly, the relative importance of the various dimers for the re-cooked L_2 sample resembled that for L_5.

However, the yields of both monomers and dimers were found to be lower in the case of the re-cooked L_2 than in the case of L_5 fraction, likely because of full exposure of L_2 to the reaction medium without protection by the carbohydrate component. It can be concluded that the effects of the organosolv cooking on the lignin structure should not be neglected.

In order to check the role of phenolic units and the occurrence of side chain reactions during the organosolv delignification, phenolic and alcoholic hydroxyl contents were determined by ^{19}F-NMR (Table 9).

It can be seen that the number of phenolic hydroxyl groups considerably decreased from L_1 to L_5, which confirms that the phenolic non-condensed β-O-4 linked guaiacyl unit (A) decreased with increasing delignification as shown by the analysis of thioacidolysis products. This phenomenon is greatly different from the case of kraft flow-through cooking in which an inverse variation trend of phenolic hydroxyl content was observed owing to extensive cleavage reactions of β-aryl ether structures.[7, 29] Thus it is also confirmed that in the course of the organosolv delignification herein the cleavage of β-aryl ether bonds was quite limited.

On the other hand, the decrease of alcoholic hydroxyl groups supported the occurrence of side chain ethylation during the organosolv delignification. This also suggests that some condensation and rearrangement reactions could be involved in this process.[12, 30]

It is interesting to note that the main effect of the re-cooking treatment revealed by the data of Table 9 was a marked decrease of the alcoholic hydroxyl groups. Despite the severe batch re-cooking, the number of phenolic hydroxyl groups was not changed by this treatment. This suggests that the variation of

TABLE 9. Phenolic (OH_{Ph}) and Alcoholic (OH_{Al}) Hydroxyl Contents of TMP Lignin Fractions.

	OH_{Ph} / C_9	OH_{Al} / C_9	OH_{Total} / C_9	OH_{Ph} / OH_{Al}
L_1	0.33	0.77	1.10	0.42
L_2	0.29	0.72	1.01	0.42
L_3	0.24	0.67	0.91	0.35
L_4	0.20	0.60	0.80	0.32
L_5	0.16	0.50	0.66	0.31
L_2 R	0.29	0.40	0.69	0.72

L_2 R: L_2 after re-cooking

phenolic hydroxyl contents in the five lignin fractions could not be due to the effect of the organosolv cooking but to the solubility of lignin fragments going into the solution at different stages of the delignification. So the level of phenolic hydroxyl content would be an important factor governing the dissolution of lignin in the organosolv fractionation.

CONCLUSION

Extraction of lignin from mechanical pulp (TMP) was performed in a flow-through reactor using an organosolv medium (ethanol-water 1:1 v/v) under acidic conditions (0.1 M acetic acid) at 175 °C. In such a process about 70 % of the lignin was extractable and recovered in five successive fractions according to the delignification time. The lignin fractions recovered by water precipitation represented about 70 % of the total extracted lignins. Furthermore, the following was demonstrated:

- Bleaching and photoyellowing of TMP did not modify the lignin extractability, which suggests that under the conditions used these treatments did not change the bonding pattern of the lignin macromolecule to a great extent.

- A more pronounced extraction was observed when the TMP process had been carried out after sulfonation (CTMP process). Introduction of sulfonic acid groups was responsible for this effect.

From the results of lignin characterization, it could be concluded that the organosolv flow-through process allowed isolation of a lignin sample which underwent limited modification, contrary to what would have happened in batch cooking, thus remaining as a whole representative of the original lignin in wood or pulp. Particularly, β-aryl ether structures were not broken down to a large extent.

However, among the five lignin fractions there existed some differences in the frequency of the main interunit linkages and the content of phenolic and alcoholic hydroxyl groups. These structural variations could be due to both lignin heterogeneity in wood (or TMP) and chemical reactions brought about by the ethanol-water medium.

EXPERIMENTAL

1. Pulp Sample Preparation

Spruce thermomechanical pulp (TMP) and the corresponding bleached (BTMP) and photoyellowed (YBTMP) samples were prepared as previously described.[1] A chemithermomechanical pulp (CTMP) was prepared in otherwise identical conditions as TMP with addition of a chemical treatment prior to defibration: 6% of Na_2SO_3, 0.4% of DTPA (based on oven-dried wood chips), and 15 min of reaction time.

2. Delignification Procedure

The flow-through reactor system and its utilization have been previously described.[6,7] About 20 g of air-dried spruce wood platelets or pulps exhaustively pre-extracted by ethanol-benzene (1:2 v/v), together with a certain amount of fine Teflon cylinders, were placed in a flow-through reactor of 250 ml total volume

(about 100 ml free volume for liquid). Flow of the solvent (ethanol-water 1 : 1 v/v, 0.1 M acetic acid) through the reactor was about 24 ml / min, corresponding to 4 min mean residence time inside the reactor. In order to obtain lignin fractions in amounts sufficient for characterizations, numerous delignification runs were performed under identical conditions: temperature 175°C, time 5 hours including about 30 min heat-up time. At the end of the given reaction time, the reactor was quickly taken out from the bath and immersed in cold water. The delignified materials were transferred into a filter and washed thoroughly with ethanol and distilled water. The residual pulps were air-dried. Weight and lignin content (Tappi standard method T 222 os-74) were determined.

3. Recovery of Organosolv Lignins

For each pulp sample, the solutions from the reactor were collected in five successive fractions. Each fraction was treated as follows. When most of the ethanol had been removed by vacuum evaporation, light brown precipitates of water-precipitable lignin (L_1 - L_5) were formed. These precipitates were separated from the solution by centrifugation for 15 min at 10, 000 rpm, and then washed several times with distilled water. Between each washing, the precipitates were settled and recovered by centrifugation. The final aqueous suspensions were then freeze-dried. The solutions, together with the washings, were submitted to vacuum evaporation and then freeze-drying. The recovered solid materials (S_1 - S_5) contain water-soluble lignins and dissolved carbohydrates.

4. UV and IR Analyses

The UV absorbances at 280 nm of the delignification solution were measured in a Beckman DU-64 spectrometer. The IR spectra of water-precipitable fractions L and water-soluble fractions S were recorded on a Perkin-Elmer IR 782 spectrometer from KBr pellets (2 - 3 mg sample / 300 mg KBr).

5. Elemental Analysis and Alkoxyl Group Content

The carbon, hydrogen and oxygen analyses were performed at the Service Central d' Analyse CNRS (Lyon). The sulphur content was determined at the Service Central d' Analyse of CTP Grenoble. The methoxyl and ethoxyl analyses were performed according to Girardin and Metche.[31]

6. Thioacidolysis

The permethylation of pulps and isolated lignins with diazomethane and the thioacidolysis of original or CH_2N_2-methylated samples were performed according to Lapierre et al.[13, 23] The main recovered monomers were quantified by GC of their trimethyl-silylated (TMS) derivatives. The thioacidolysis dimers were analysed after Raney nickel desulfuration.[14] Standard errors between duplicate experiments were 5 % and 10 % for the monomeric and dimeric products, respectively.

7. ^{19}F-NMR Determination of Hydroxyl Groups

Lignin samples were turned into their 2-fluorobenzoic ester derivatives and then subjected to ^{19}F-NMR analysis following the method proposed by Barrelle.[32]

8. Re-cooking Experiment

200 mg of TMP L_2 sample were dissolved with 200 ml ethanol-water (1 : 1 v/v) containing 0.1 M acetic acid in the flow-through reactor (flow of solution = zero). Temperature was raised from 80 to 175 °C in a period of 30 min then maintained at 175 °C for 2 hrs. After cooking, the resulting lignin sample was totally recovered by evaporation of the ethanol and then freeze-dried.

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