

# Characterization of Residual Lignins from Chemical Pulps of Spruce (*Picea abies*) and Beech (*Fagus sylvatica*) by $\text{KMnO}_4$ Oxidation\*<sup>1</sup>

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## ABSTRACT

The enzymatic isolation of residual lignins obtained from spruce and beech pulps (obtained by sulfite, kraft, ASAM and soda/AQ/MeOH pulping processes) and their characterization was described in previous publications. Here, the residual lignins have been submitted to potassium permanganate oxidation ( $\text{KMnO}_4$  degradation), and 9 aromatic carboxylic acids (3 of them are dimeric) were identified after methylation with diazomethane by GC/MS. The analytical challenge during quantification by the internal standard methods was the partly high protein content of the samples, which resulted in elevated anisic acid yields in the degradation mixture of sulfite residual lignins. The results are compared with the  $\text{KMnO}_4$  degradation of the corresponding MWLs and discussed in terms of S/G ratios and degrees of condensation. The latter was calculated as a quotient between the aromatic carboxylic acids derived from condensed and non-condensed lignin structures. Typical degradation patterns for the various processes have been observed. Among other parameter, the relative compositions between *iso*-hemipinic acid (which is for condensation in pos. 5 of the aromatic ring) and *meta*-hemipinic acid and 3,4,5-trimethoxyphthalic acid (both are for condensation in pos. 6 of the aromatic ring) was found to be process specific. Kraft and soda/AQ/MeOH residual lignins yielded higher amounts of *iso*-hemipinic acid. In contrast, the relative yields of *meta*-hemipinic acid and 3,4,5-trimethoxyphthalic acid (the latter in beech lignins) are higher in sulfite and particularly in ASAM residual lignin. In case of beech residual lignins the amount of acids originated from non-condensed syringyl type lignin units was surprisingly high. The condensation degree of residual lignins was shown to be generally higher than that of MWLs. This was especially true for the G units. ASAM residual lignin exhibited very high S/G ratios and degrees of polymerization. Causality between condensation degree and total yield of degradation products was demonstrated.

*Keywords* : residual lignins from sulfite, kraft, ASAM soda/AQ/MeOH pulps, MWL, potassium permanganate oxidation, condensation degree, S/G ratios in lignins

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## 1. INTRODUCTION

In previous publications (Choi and Faix, 1998 and 1999; Choi *et al.* 2001) the isolation and characterization of residual lignins was presented, which are left in spruce and beech pulps after applying the following processes: magnesium bisulfite pulping (shortly: sulfite), a traditional sulfate pulping (kraft), alkaline-sulfite-anthraquinone-methanol pulping (ASAM), and soda-anthraquinone-methanol pulping (soda/AQ/MeOH). The enzymatic hydrolysis approach was used for lignin isolation procedure. One advantage of this technique is in comparison with the acid hydrolysis approach is the avoidance of low pH and, consequently, the prevention of secondary reactions (formation of novel C-C linkages) during isolation. A second benefit is the high yield of isolates. On the other hand, the analysis of the products is affected by enzymatic proteins attached inseparably to the samples. This detrimental effect is especially high in case of residual lignins isolated from sulfite pulps.

The previous publication of Choi *et al.* (2001) described the analytical pyrolysis and the analytical challenge to cope with complex mixtures of residual lignins and polysaccharides in presence of high amounts of proteins.

Aiming at an in-depth analysis of residual lignins in terms of the frequency of chemical bonds between the aromatic rings, we present here the results of potassium permanganate oxidation. This traditional technique of lignin depolymerization is known since the pioneering work of Freudenberg *et al.* (1936).  $\text{KMnO}_4$  oxidation was improved several times since that time, e. g. by Freudenberg *et al.* (1962). The early results obtained on spruce lignin are summarized by Freudenberg (1968) and in general by Chang and Allan (1971).

In the following decade the technique was

further refined and the advent of modern capillary GC contributed a lot to its success. The important contributions for the improvement of  $\text{KMnO}_4$  oxidation in the seventies by Miksche and his co-worker in Sweden was reviewed by Gellerstedt (1992) in the widely distributed book among wood chemists "Methods in Lignin Chemistry". The experimental process consisting of methylation with dimethylsulfate, oxidation with  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$ , and methylation with diazomethane for GC analysis was first published in the papers of Erickson and Miksche (1972) and Erickson *et al.* (1973a, 1973 b). Gellerstedt (1992) recommends this technique with small modifications. We adopted his version as many research laboratories did in the last decade.

## 2. MATERIALS and METHODS

### 2.1. Isolation of Residual Lignins

The isolation of residual lignins of unbleached sulfite, ASAM, kraft and soda/AQ/MeOH pulps from spruce (*Picea abies*) and beech (*Fagus sylvatica*) by enzymatic hydrolysis was described in a previous publication (Choi *et al.* 2001). Here it should only be recalled that the abbreviation RL1 refers to residual lignins obtained after purification of the enzymatically insoluble lignin moiety, whereas the abbreviation RL2 refers to samples obtained by acidification from the enzymatically solubilized part.

### 2.2. Potassium Permanganate Oxidation ( $\text{KMnO}_4$ oxidation)

Permanganate oxidation was performed according to Gellerstedt (1992) with a slight modification. For the first oxidation step, approximately 100 mg lignin (based on hydrolysis residues of residual lignin) was suspended in 1,2-dimethoxyethane/methanol/water (35:35:30, v/v,

10 ml) during 20 h under  $\text{N}_2$ . The pH of the reaction mixture was maintained at 11 with 15% KOH using an automatic titration apparatus. The second oxidation step was carried out with 30% hydrogen peroxide for 10 min at  $50^\circ\text{C}$ . The aromatic carboxylic acids released from lignins were methylated with diazomethane and the resulting aromatic carboxylic acid methyl esters were separated by GC on a column DB-1701 (60 m  $\times$  2.25  $\mu\text{m}$ ) and identified by GC/MS. Temperature program: 3 min isothermal at  $45^\circ\text{C}$ , heating rate of  $3^\circ\text{C}/\text{min}$  until the final temperature of  $280^\circ\text{C}$  which was maintained for 60 min. Pyromellitic acid methyl ester was used as internal standard. The response factors (RF value) for quantitation of the H, G, and S type degradation products were calculated based on the authentic compounds anisic acid (H type, RF = 1.78), veratric acid (G type, RF = 1.41), and 3,4,5-trimethylphthalic acid (S type, RF = 1.14). The enzyme used for enzymatic hydrolysis was also submitted to  $\text{KMnO}_4$  oxidation, and as expected anisic acid was obtained. Taking into consideration the protein content of residual lignins (Choi *et al.* 2001) and the conversion rate of protein to anisic acid, the results were corrected in terms of this acid according to Fig. 1 and the equation shown there.

### 3. RESULTS and DISCUSSION

#### 3.1. Identification and Yield of Aromatic Carboxylic Acids

The identified and methylated carboxylic acids yielded by potassium permanganate oxidation are presented in Fig 2 together with their code numbers as suggested by Gellerstedt (1992). In top of Fig. 2 the acids are depicted, which arise from non-condensed lignin polymers possessing only one carboxylic group in *para* position to the original  $\text{OH}_{\text{phen}}$  group (anisic acid [no. 1],

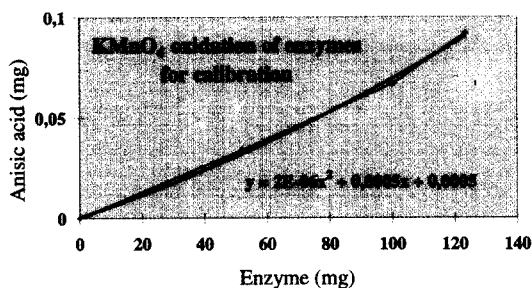
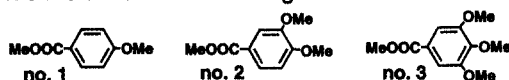


Fig. 1.  $\text{KMnO}_4$  oxidation of enzymes used for enzymatic hydrolysis of pulps. Correlation between the yield of anisic acid and protein amount submitted to oxidation.

#### non-condensed degradation acids:



#### condensed degradation acids:

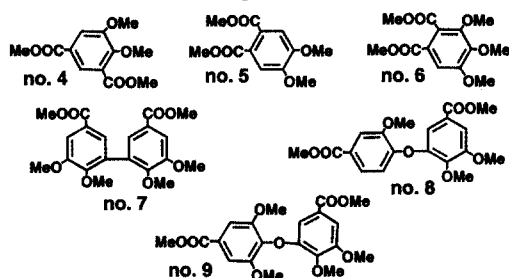


Fig. 2. Aromatic carboxylic acid methyl esters obtained by  $\text{KMnO}_4$  oxidation of residual lignins with their code numbers used in this publication

veratric acid [no. 2], 3,4,5-trimethoxybenzoic acid [no. 3]). On the other hand, *iso*-hemipinic acid [no. 4], *meta*-hemipinic acid [no. 5], 3,4,5-trimethoxyphthalic acid [no. 6], and three dimeric compounds dehydrodiveratric acid [no. 7], (2,3,3'-trimethoxy-5,4'-diphenylether-dicarboxylic acid [no. 8], and 3,4,3'5'-tetramethoxy-4,5-diphenylether-dicarboxylic acid [no. 9]) are typical for "condensed" units (Fig. 2, bottom). The term "condensed" means in this context that the aromatic rings are bonded within the macromolecule with additional chemical linkages as indicated by a second  $\text{COOH}$  group in monomeric

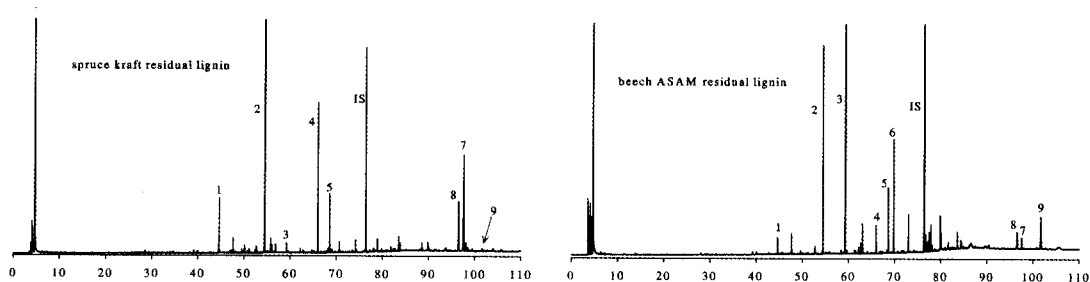


Fig. 3. Gas chromatographic separation of aromatic carboxylic acid methylesters obtained by potassium permanganate oxidation of residual lignins.

Table 1. Yields and relative amounts of essential aromatic carboxylic acids obtained by  $\text{KMnO}_4$  oxidation of residual lignins in comparison to those of corresponding MWLs. The code numbers 1 to 9 refer to the compounds shown in Fig. 2.

Samples	Total yield % (w)	Aromatic carboxylic acid methylesters (see Fig. 1) in relative mol %									S/G ratio	Degree of condensation	
		non-condensed			condensed							total	G
		1	H 2	G 3	4	G 5	G 6	S 7	G 8	G 9			
SPRUCE: MWL (Reference)	39.9	2.2	53.9	7.9	8.5	4.5	6.0	5.5	10.5	1.0	0.17	0.56	0.55
sulfite RL2 <i>normalized*</i>	5.9	33.8 2.2	34.0 49.7	1.6 2.3	8.3 12.1	12.5 18.3	0.0 0.0	5.5 8.0	4.3 6.3	0.0 0.0	<i>tr.</i>	0.84	0.89
kraft RL1 <i>normalized*</i>	11.1	3.7 2.2	54.3 55.1	0.7 0.7	12.3 12.5	4.9 5.0	0.0 0.0	7.5 7.6	15.9 16.1	0.6 0.6	<i>tr.</i>	0.72	0.75
ASAM RL2 <i>normalized*</i>	5.3	8.1 2.2	42.5 45.2	0.0 0.0	9.6 10.2	17.0 18.1	0.0 0.0	10.0 10.6	12.8 13.6	0.0 0.0	<i>tr.</i>	1.11	1.16
soda/AQ/MeOHL1 <i>normalized*</i>	12.5	3.2 2.2	57.1 57.7	0.4 0.4	12.3 12.4	3.9 3.9	0.0 0.0	8.0 8.1	14.6 14.7	0.7 0.7	<i>tr.</i>	0.65	0.68
BEECH: MWL (Reference)	31.3	1.5	41.2	39.4	3.4	3.8	0.0	2.1	2.6	6.0	0.74	0.22	0.43
sulfite RL2 <i>normalized*</i>	8.2	14.4 1.5	17.7 20.3	45.0 51.7	1.9 2.2	5.2 6.0	6.6 7.6	1.5 1.7	0.8 0.9	7.1 8.2	1.73	0.36	0.73
kraft RL1 <i>normalized*</i>	15.1	1.8 1.5	17.8 17.9	62.0 62.2	4.1 4.1	1.8 1.8	1.5 1.5	1.9 1.9	3.1 3.1	6.0 6.0	2.00	0.23	0.77
ASAM RL1 <i>normalized*</i>	7.0	1.1 1.5	15.3 15.2	55.6 55.4	2.1 2.1	5.0 5.0	10.3 10.3	2.4 2.4	1.6 1.6	6.7 6.7	1.68	0.24	0.95
ASAM RL2 <i>normalized*</i>	6.9	3.7 1.5	14.7 15.0	55.2 56.4	2.0 2.0	5.2 5.3	9.6 9.8	2.4 2.4	1.5 1.5	5.8 5.9	2.24	0.23	0.94
soda/AQ/MeOH RL1 <i>normalized*</i>	16.6	2.6 1.5	19.2 19.4	62.1 62.8	3.8 3.8	1.5 1.5	1.2 1.2	1.6 1.6	2.4 2.4	5.5 5.6	2.01	0.19	0.62

Explanation. *Normalized\**: was performed to avoid the elevated yield of acid no. 1 (anisic acid) due to the high protein content of sulfite residual lignins. The amount of acid no. 1 was put arbitrarily to the value found for the corresponding MWL and the relative percentages of the other acids have been recalculated. Degree of condensation. Total: sum of acids 4 to 9 divided by sum of acids 1 to 3. G: sum of acids [4G + 5G + 7G + 8G + (9G + S):2] divided by 2G (i. e. only G acids are considered).

produces or by C-C or C-O-C linkages in dimerics. The formation of *meta*-hemipinic acid is demonstrated in Fig. 5 (top).

As an example for product separation, the corresponding gas chromatograms of spruce and

beech kraft residual lignins are depicted in Fig. 3. The quantitative evaluation of all GC data are listed in Table 1, which reveals that the total yields of methylated carboxylic acids vary between 6 and 13% (spruce residual lignins)

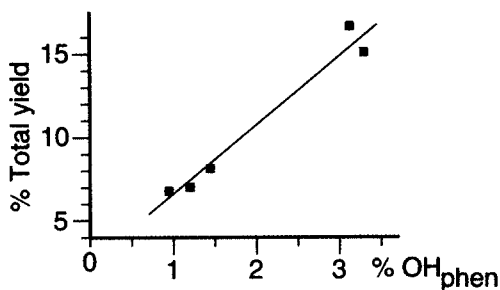


Fig. 4. Dependence of the total yield of aromatic carboxylic acid methylesters obtained by  $\text{KMnO}_4$  oxidation of beech residual lignins on their contents of phenolic OH groups (see Table 1 and text).

and between 7 and 17% (beech residual lignins), respectively. These yields are substantially lower than those obtained from the reference MWLs (39.9% spruce, 31.3% beech).

It was suggested that the phenolic OH content has a positive influence on the yields of aromatic carboxylic acid obtained by  $\text{KMnO}_4$  oxidation (Gellerstedt 1992). Trying to corroborate this hypothesis, we plotted the total acid yields versus the results of phenolic OH group determination obtained by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and  $\text{NaIO}_4$  oxidation (Choi and Faix 1998). It is obvious that the results are not satisfactory. The phenolic OH group content of the reference MWLs, for example, was found to be low in comparison with those of residual lignins and, nevertheless, the MWLs yielded more degradation products than the residual lignins. Though a certain correlation could be established for beech residual lignin (Fig. 4), in view of the scattering results for spruce residual lignins becomes clear that the  $\text{OH}_{\text{phen}}$  content is only one of parameters governing the aromatic carboxylic acid yields. The higher frequency of C-C and C-O-C bonds between the aromatic rings and the protein matrix, in which the residual lignins are embedded, exercised probably a negative effect on oxidative depolymerization of residual lignins.

### 3.2. Influence of Enzymatic Proteins to Quantification

For the sake of easy comparability of the yields of the 9 degradation products, the results are presented as relative mol % on Table 1. In this context, the yield of anisic acid [no. 1] deserves a special attention. As far as the sulfite residual lignins from spruce and beech are concerned, unusual high contents of anisic acid (33.8% for spruce and 14.4% for beech) were observed. If the samples would not contain protein, this observation could be interpreted as an indication of high contents of *p*-hydroxyphenylpropane (or -phenylmethane or -phenylethane) units in the lignin (short: H units).

However, remembering the well established fact that demethoxylation is not a predominant reaction during sulfite pulping (Gierer 1982) and in view of the low anisic acid amounts found in the product mixture of the reference MWLs (1.5-2.2%), the following may safely be concluded: The correction equation used for the detrimental effect of protein (presented in the Experimental Part, Fig. 1) failed both for spruce and beech sulfite residual lignins because of their high protein contents. Thus the elevated anisic acid yields found for these lignins are probably artifacts due to the tyrosine moieties of the protein (Fig. 5). This finding is analogous to that reported in our previous paper (Choi *et al.* 2001) concerning the elevated yields of phenol and cresol obtained by analytical pyrolysis in protein rich samples.

This is the reason why we decided to apply a second normalization step aiming at the elimination of the disturbing effect of the anomalous high anisic acid content of the sulfite residual lignins. To this purpose, the anisic acid content of all residual lignins was set arbitrarily to that of the corresponding MWLs and the relative ratios of degradation products have been recalculated, in the course of which the

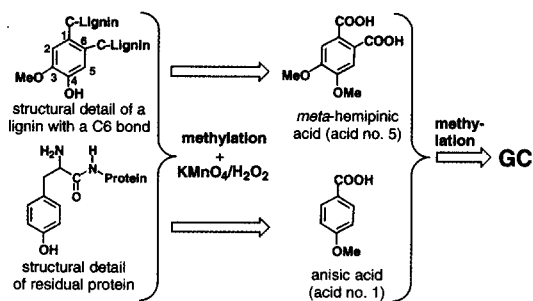


Fig. 5. Two examples for  $\text{KMnO}_4$  oxidation. *Top*: Conversion of a G unit involved in a C6 linkage into *meta*-hemipinic acid. *Bottom*: Conversion of the tyrosine moiety of a protein in anisic acid. This reaction is responsible for the elevated anisic acid yields obtained from oxidation of sulfite residual lignins.

relative compositions of degradation mixtures obtained from lignins with high protein content are readjusted to a normal H content. Only samples with anomalously high protein content show essential changes after this calculation. This normalization step permits a better comparability of the aromatic carboxylic acids yields between samples with low and high protein content.

### 3.3. S/G Ratios of the Aromatic Carboxylic Acids

The summative parameters i) S/G ratios and ii) degrees of condensation derived from the normalized data are worthwhile for a consideration in detail. The yield of S type degradation acids from spruce MWL are low but not negligible. The sum of 3,4,5-trimethylbenzoic acid (7.9%), 3,4,5-trimethylphtalic acid (6%) and of the dimeric GS acid no. 9 (1.0 : 2 = 0.5%) amounts to 14.4%. Freudenberg (1968) summarized his lifetime research on spruce lignin with the statement that the G lignin of this tree may contain up to 5.5% of S units. Considering the fact that the results of our

Table 2. S/G ratios of residual lignins from several beech chemical pulps

Beechwood lignins	S/G by analytical pyrolysis corrected	S/G non-corrected from Tab. 1
MWL	0.75	0.74
sulfite RL1	0.77	1.73
kraft RL1	0.68	2.00
ASAM RL1	1.12	1.68
ASAM RL 2	1.02	2.24
soda/AQ/MeOH	0.66	2.01

$\text{KMnO}_4$  oxidation are not corrected for the well known over biased S content of all kind of degradation experiments, it can be deduced that S content of the spruce MWL is in a regular range. Not unexpectedly, the S content of the residual lignins is practically eliminated due to the easy degradability of S lignins during pulping.

Choi *et al.* (2001) accounted for S/G ratios of beech residual lignins by analytical pyrolysis, which are listed in Table 2 together with the uncorrected S/G ratios from Table 1.

This compilation provides evidence that the uncorrected data of  $\text{KMnO}_4$  oxidation are on an average 2.4 times higher than the corrected S/G data of pyrolysis, being the lowest factor (1.5) for ASAM RL1 and the highest factor (3.0) for soda/AQ/MeOH. The higher yields of S type degradation products with a factor between 2 and 3 are well known since a long time (Sarkanen and Hergert 1971). Our data are an additional confirmation of similar findings frequently described in the literature.

Surprising is, however, that the uncorrected S/G ratio of beech MWL obtained by  $\text{KMnO}_4$  oxidation (0.74) is very similar to the corrected S/G ratios obtained by analytical pyrolysis (0.75). A note of caution should be the corollary of this observation: There are no universal

conversion factors, and all conversion factors of this type should be used with a critical sense. Nevertheless, it can be deduced that the S content of residual lignins - at least of that part, which is susceptible for degradation - is surprisingly high. Of course, the low total yields, which amounts to  $\frac{1}{2}$  to  $\frac{1}{4}$  of that of MWLs, exerts a considerable limitation to generalization of this finding.

### 3.4. Condensation Degrees and Process Specific Degradation Products

A data evaluation in terms of non-condensed and condensed units also leads to interesting insights. To this purpose, the degrees of condensation (DCs) as quotients of condensed and non-condensed degradation products has been calculated (Table 1). This calculation was done twice: First, including all types of degradation products (all H, G, and S units) leading to total DCs, and second, taking into consideration only the G units leading to G-DCs.

For spruce lignins the total DC and G-DC values are, of course, essentially identical. The G-DCs are increasing from 0.55 (spruce MWL) on an average to 0.87 being the lowest value (0.68) for soda/AQ/MeOH and the highest (1.16) for ASAM RL2. This observation is in agreement with the view that condensed lignin structures are difficult to split during the reductive conditions of a digestion. Thus they are enriched in residual lignins. On the other hand, secondary reactions can also occur in the course of which new C-C and C-O-C linkages to the aromatic rings may be formed. The enrichment of condensed moieties in spruce residual lignins are well manifest by elevated yields of *iso*-hemipinic acid and *meta*-hemipinic acid (exception soda/AQ/MeOH lignin), which are for condensation reactions in position 5 and 6, respectively. In residual lignins of sulfite and

ASAM pulping, the increment of *meta*-hemipinic acid is marked. This can be taken as a specific feature of secondary reactions in presence of  $\text{SO}_3\text{H}$  or  $\text{SO}_3^{2-}$  anions.

The increased frequency of the dimeric degradation product no. 8, which is for 4-O-5 linkages, is also clearly perceptible with the exception of sulfite RL2 residual lignin. The high yield of dimeric degradation product no. 7, which is for 5-5 linkages in biphenyl units, is especially remarkable for the ASAM RL2 lignin. Altogether, the matrix of degradation acids for spruce lignins is a confirmation for the fingerprinting ability of  $\text{KMnO}_4$  degradation, which is, in turn, a confirmation of the particular degradation mechanisms and secondary reactions of the various pulping processes.

Concerning the G-DC data of beech lignins in Table 1, the most striking observation is the very substantial decrease of veratric acid (no. 2, representing non-condensed G unit) from 41 to approx. 17.6%. Moreover, the high yield of 3,4,5-trimethoxybenzoic acid (57.7%) indicates a high participation of non-condensed S units on the residual lignins. The limitations of this finding due to the low yields were already discussed above.

In comparison of the G-DC value of MWL (0.43), the residual lignins of beech suffered a condensation degree increment to an average G-DC of 0.8. The change in condensation degree is not readily visible when the S units are also included into the calculation because of the high yield of 3,4,5-trimethylsyngic acid that disguise the results. In harmony with the observation on spruce lignin series, the G units of ASAM residual lignins reveal the highest degree of condensation (0.94 - 0.95), whereas the other residual lignins exhibit average G-DC values of 0.71.

Another peculiarity of ASAM residual lignins is the high yield (9.8 to 10.3%) of 3,4,5-

Spruce:

<b>Yields %</b>	MWL (39.9)	>	soda/AQ/MeOH (12.5)	>	Kraft RL1 (11.1)	>	sulfite RL2 (5.9)	>	ASAM RL2 (5.3)
<b>G-DCs</b>	MWL (0.5)	<	soda/AQ/MeOH (0.68)	<	Kraft RL1 (0.75)	<	sulfite RL2 (0.89)	<	ASAM RL2 (1.16)

Beech:

<b>Yields %</b>	MWL (31.3)	>	soda/AQ/MeOH (16.6)	>	Kraft RL1 (15.1)	>	sulfite RL2 (8.2)	>	ASAM RL1 (7.0)	≈	ASAM RL2 (6.9)
<b>G-DCs</b>	MWL (0.43)	<	soda/AQ/MeOH (0.62)	<	sulfite RL2 (0.73)	<	Kraft RL1 (0.77)	<	ASAM RL1 (0.94)	≈	ASAM RL2 (0.95)

trimethoxyphtalic acid [acid no. 6], which is the S-analog to *meta*-hemipinic acid found in elevated yields in sulfite and in ASAM residual lignins. Kraft and soda/AQ/MeOH lignins of beech yielded only 1.5 to 1.2% of acid no. 6, respectively. However, sulfite RL2 sample gives rise already to 7.6% of this acid. This findings are additional proves for the preponderance of condensation reactions in position 2 (G units) or 2/6 (S units) in the course of these processes.

The sequences of spruce and beech lignins are presented in the following both in terms of their total yields of degradation acids and their condensation degrees (G-DCs) in decreasing and increasing order, respectively.

As demonstrated above, the sequences concerning yields and condensation degrees (G-DC) results in the same succession. A change in the order of soda/AQ/MeOH and sulfite lignin in case of G-DCs of beech lignin do not contradict to this finding since the G-DC values in question are very similar (0.73 and 0.77). Accordingly, the condensation degree of G units seems to exert a great influence on the total yield of acids.

#### 4. CONCLUSION

Potassium permanganate oxidation is one of the useful lignin degradation methods to predict the degree of condensation in lignin polymers.

C-C condensed linkages are originally present in native lignin or newly produced by secondary reaction during pulping process (splitting and condensation). ASAM lignins show the highest value of condensation degree, and the lowest value in the Soda/AQ/MeOH procedure in both wood species.

The positional preferences for condensation reaction can be envisaged by the relative composition of degradation products obtained. Based on the data, the condensation reaction could be proceeded via C5 positions under alkaline pulping condition. However, sulfite and ASAM pulpings elevated the yields of condensed units on C6 position.

It is not clear in the moment, why alkaline sulfite cooking in the presence of AQ and MeOH (i. e. ASAM process) further promotes this type of condensation reaction that is not especially effective in case of alkaline pulping condition.

Even though the S/G value of beech MWL was estimated to approximately 0.7, those of residual lignins gave the values between 1.7 and 2.2, indicating that the phenolic hydroxyl groups are not evenly distributed between syringyl and guaiacyl units in beech residual lignins.

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