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**CHARACTERIZATION OF LIGNINS FROM ORGANOSOLV  
PULPING ACCORDING TO THE ORGANOCELL PROCESS**

**PART 4. PERMANGANATE OXIDATION AND THIOACIDOLYSIS**

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**ABSTRACT**

Soluble and residual spruce lignins were subjected to permanganate oxidation and thioacidolysis to elucidate changes in lignin's structure during Organocell pulping.

As expected degradation reactions known from soda pulping are dominant especially in stage 2, including extensive enol ether formation. The chemical effect of methanol appears to be restricted to a minor methylation of the  $\alpha$ -C-atom which prevents quinone methide formation and thus suppresses subsequent condensation reactions. Other beneficial effects of methanol such as liquor diffusion into the chips and a better lignin solubility obviously contribute to the successful delignification of softwoods in Organocell pulping.

### INTRODUCTION

A comprehensive characterization of lignin requires a variety of different analytical data including elemental composition, functional group determination, sugar composition, molecular weight distribution and degradation reactions. While the former parameters were discussed in the first three parts of this series<sup>1-3</sup>, interest now focuses on degradation reactions, which are particularly informative for elucidating changes concerning lignin's structure during pulping. The use of both permanganate oxidation and thioacidolysis proved instructive for interpretation purposes.

Both residual lignins and soluble lignins from 20 l batch cookings according to the Organocell process were subjected to permanganate oxidation (PO)<sup>1</sup>. PO is well suited for estimating the different types of interunit linkages provided the aromatic nucleus is involved<sup>4,5</sup>. The loss of information concerning side-chain structure on account of complete oxidation, the restriction to originally phenolic units and the sequence of several time-consuming steps during the analysis are however serious drawbacks in the use of PO.

Four lignins isolated from the pulping liquor were furthermore analyzed by means of thioacidolysis, which, at least at the present level of development, is restricted to the inclusion of noncondensed structures only<sup>6</sup>. However the relative ease with which the experimental steps are performed, complete sidechain preservation and high yields make thioacidolysis a very promising method for lignin degradation.

At first sight the Organocell process looks like a combination of the classical alcohol/water delignification according to Kleinert<sup>7</sup> (first stage) and a modified soda process (second stage)<sup>8</sup>. Neither of these processes is suited to effective softwood pulping. Taking Gierer's reaction mechanisms as a basis for discussion, neither the first nor the second stage should be able to cleave the important phenolic  $\beta$ -0-4 linkages, thus preventing 'lignin peeling'<sup>9</sup>. Nevertheless, Organocell pulping permits a delignification of softwoods down to kappa numbers of about 30<sup>8</sup>. The question must arise therefore whether the undisputedly superior delignification of the second stage in comparison to conventional soda pulping can be explained on the basis of specific chemical reactions occurring in the lignin during Organocell pulping, or whether the additional methanol does not involve reaction mechanisms but has a nonspecific, mainly physical influence (e.g. improved lignin solubility, high pressure during delignification, different penetration of the liquor into the chips).

## EXPERIMENTAL

### Origin of the lignins

The Organocell process was simulated in a 20 l batch digester with liquor circulation<sup>1</sup>. Starting at 0 min (moment when the heat-up phase was over) samples from both the liquor (soluble lignins) and the cooking residue (residual lignins) were taken at 10 min intervals. Second stage lignins had been pretreated with a first stage cook (40 min). Spruce chips of industrial size were used throughout the experiments. The iso-

lation of the soluble lignins is described elsewhere<sup>1</sup>. The denomination of the cooking stage (1S or 2S) is followed by the cooking time expressed in minutes. Suffix 'R' stands for cooking residue.

Examples:

1S/10: soluble lignin, first stage, 10 min.

2S/20 R: cooking residue, second stage, 20 min.

#### Permanganate oxidation

Permanganate oxidation was performed according to Erickson et al.<sup>10</sup>. Calculation of the frequency of occurrence of the main structural units is thoroughly described by Larsson and Miksche<sup>4</sup>. In accordance with this original calculation method the values obtained by PO are expressed in mol % in contrast to thioacidolysis. An oxidation yield of 60 % per carbon substituent at the aromatic ring was assumed. Phenolic OH groups were either ethylated (72 h) or methylated (24 h), using diethylsulfate and dimethylsulfate, respectively. During oxidation of cooking residues, extra portions of  $\text{KMnO}_4$  were added as described by Gellerstedt and Gustafsson<sup>11</sup>. Separation of the ester mixtures and quantification of the monomers and dimers was accomplished by means of GC using a 25 m fused silica column (OV 1, Carlo Erba) and a temperature program of 5°C/min from 150°C to 280°C.

#### Thioacidolysis

Thioacidolysis reactions were carried out as described by Lapiere et al.<sup>6</sup>, except that the analyses were partially run on the above GC column.

## RESULTS AND DISCUSSION

### Permanganate Oxidation:

It is well known that PO is not a highly selective procedure and is restricted to structural units with originally free phenolic OH groups, unless lignin is pretreated by CuO oxidation or other appropriate degradation reactions<sup>5</sup>. Technical lignins from alkaline pulping processes are rich in OH<sub>phen.</sub> groups<sup>9</sup> so that the oxidation products of PO may be considered representative of both phenolic and etherified structural units (Figure 1). In the case of MWL and residual lignins with short cooking times (1S/20 R, 1S/40 R), however, low oxidation yields (on account of low OH<sub>phen.</sub> contents) render interpretation of the results less reliable. Additional measures for increasing oxidation yields of these samples were not taken, as identical treatment of all samples was considered essential.

The highest concentrations of compound I, (Figure 2, Table 1) representing noncondensed p-hydroxyphenyl units can be traced in first stage lignins from the spent liquor, suggesting an initial release of such structures. Unfortunately standards for condensed p-hydroxyphenyl units were not available so that the influence of condensation reactions on the decreasing concentrations of compound I could not be pursued.

Compound II, originating from noncondensed guaiacyl end groups, is by far the most abundant oxidation product. Both residual and soluble lignins show very similar changes in the frequency of occurrence

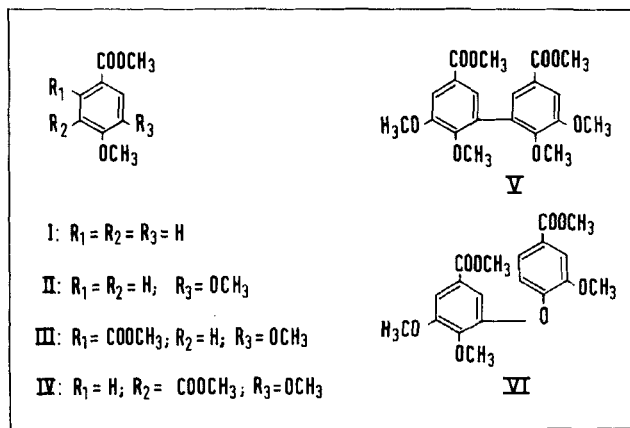


FIGURE 1: Main degradation products (I - VI) from PO

during the cook. Concentrations of compound II are consistently higher in soluble lignins, indicating a better solubility and/or an intensified ether cleaving activity in the noncondensed lignin portions. The distinct decrease at the onset of stage 2 may arise from condensation reactions at the C5-atom (see compound IV) and a better solubility of condensed structures in the alkaline medium. Unfortunately, enol ethers, i.e. structures which are formed to a considerable extent<sup>9</sup> in sodalike pulping processes also give rise to compound II during PO so that especially in the second stage the frequency of occurrence of noncondensed guaiacyl end groups are certainly lower than evaluated by PO.

High concentrations of the metahemipinic acid derivative (compound III) may be considered unique for first stage lignins according to the Organocell process. Phenylpropane units with an additional linkage at the C6-atom ( $\alpha$ -6;  $\beta$ -6) are rare in native lignins, usually not above 4 - 4.5 %<sup>12</sup>, so that the 14.1 % of

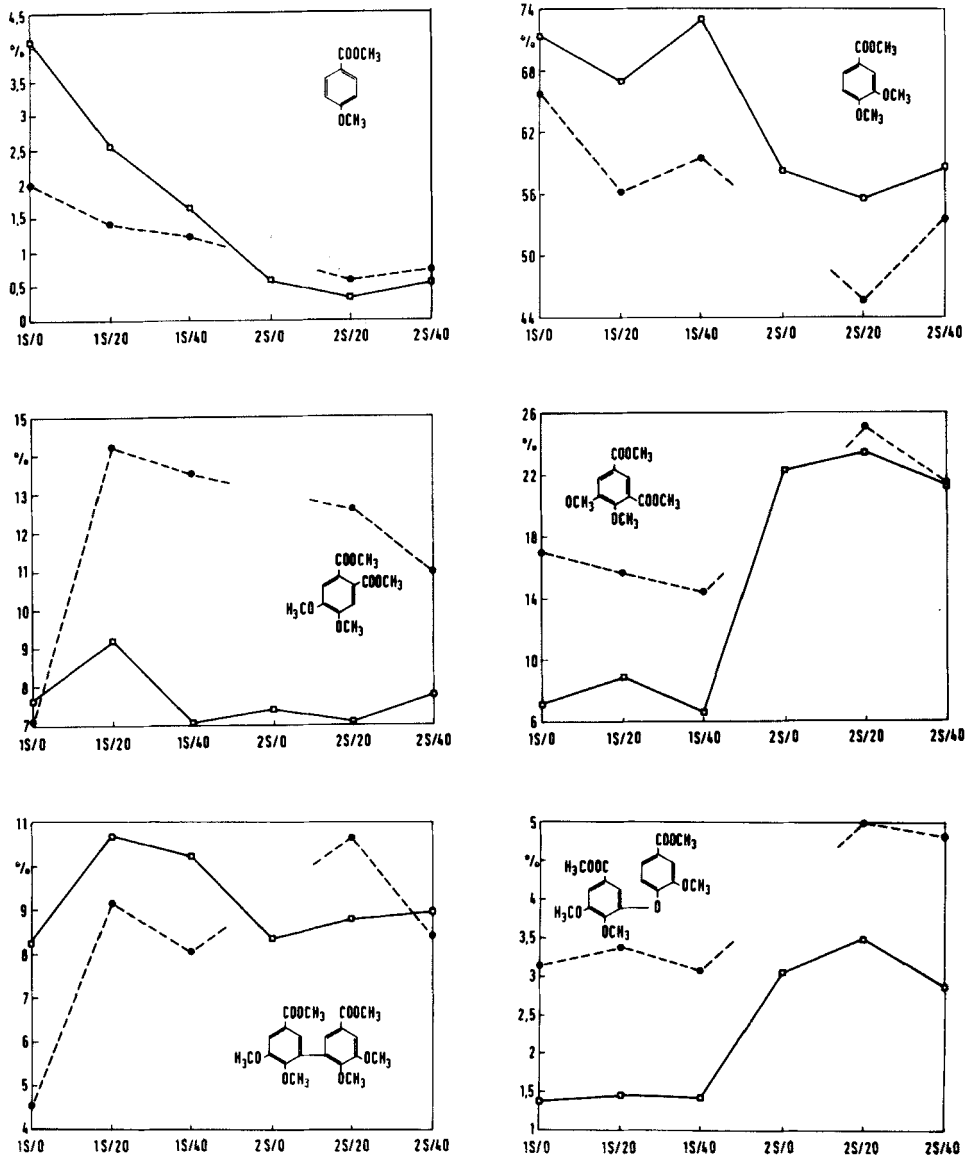


FIGURE 2: Amounts of main degradation products (PO, compounds I - VI).  
 Solid line: soluble lignins  
 Dotted line: residual lignins



TABLE 1

Frequency of Occurrence of Phenolic Phenylpropane Units (mol %) as Evidenced by the Analysis of the Most Abundant Oxidation Products.

Sample	Frequency of Occurrence					
	I	II	III	IV	V	VI
1S/0	4.1	71.4	7.7	7.2	1.4	8.2
1S/20	2.6	67.1	9.2	8.9	1.5	10.7
1S/40	1.7	73.0	7.0	6.7	1.4	10.2
2S/20	0.6	58.2	7.4	22.3	3.7	8.8
2S/40	0.6	58.5	7.8	21.2	2.9	9.0
MWL	2.0	65.8	7.2	17.2	3.2	4.6
1S/20 R	2.0	56.1	14.1	15.5	3.8	9.1
1S/40 R	1.2	59.5	13.6	14.4	3.1	8.2
2S/20 R	0.6	45.8	12.7	25.1	5.1	10.7
2S/40 R	0.7	53.6	11.0	21.5	4.8	8.4

1S/20 R must be assigned to secondary reactions involving the C6-atom. However, condensation reactions during the soda and kraft processes usually take place at the C5-atom (see compound IV), leaving out C2 and C6<sup>9</sup>. Considering the acidic pH of the first stage (pH 4 - 4.5)<sup>8</sup>, condensation reactions may give rise to  $\alpha$ -6 structures<sup>13</sup>, which in turn form compound III during PO. The exclusive participation of phenolic units in this type of reaction certainly emphasizes the frequency of occurrence of compound III, as the underlying idea of the quantitative calculation - i.e. the representativity of the phenolic units for the total of

phenylpropane units - is no longer valid. No matter to what extent the occurrence of condensation reactions involving the C6-atom and quinone methide intermediates at the onset of the first stage is evident.

Condensation reactions in the C5-atom which are common in alkaline pulping processes<sup>9</sup>, presumably occur in the second stage of the Organocell process, as shown by the distinct increase of compound IV in both soluble and residual lignins at the beginning of stage 2. However, interpretation is complicated by the fact that stilbenes and monophenolic biphenyls are also potential sources for compound IV<sup>11</sup>. Besides, as mentioned above, the enhanced solubility on account of the alkaline medium of the second stage may increase concentrations of condensed structures. The correlation between compounds IV and V, described by Gellerstedt and Gustafsson<sup>11</sup>, which says that increasing amounts of biphenolic biphenyls (compound V) should go hand in hand with increasing portions of monophenolic biphenyls in compound IV, appears to be acceptable for residual lignins, where concentration patterns for compounds IV and V are quite similar. It can hardly be applied to soluble lignins, where changes in frequency of occurrence have an opposite tendency.

As is the case with the other oxidation products representing condensed structures, the highest amounts of compound VI, which originates from phenylpropane units connected by 4-0-5 linkages were found in residual lignins. With a maximum of 5 % (2S/20 R), however, this oxidation product plays only a minor role.

#### Thioacidolysis:

First stage lignins have been claimed to be only slightly degraded on account of the mild reaction

conditions applied. High portions of coniferyl aldehyde and coniferyl alcohol end groups, found at the end of the first stage confirm this assumption and may be further due to an enrichment of these structures by endwise cleavage of low molecular weight fragments (Table 2). Nevertheless, first stage lignins display the typical features of technical lignins such as enol ether formation (Table 2) and condensation reactions of the  $\alpha$ -6 type (see above).

The onset of the second stage is accompanied by massive enol ether formation, by a distinct decrease in noncondensed guajacyl units and coniferyl alcohol groups and by the complete disappearance of the labile coniferyl aldehyde groups. The decrease of the main degradation product which indicates a reduction of noncondensed structures with a  $C_3$ -side chain is due to condensation reactions on the one hand (confirmed by  $KMnO_4$  oxidation) and on the extensive enol ether formation on the other hand. It is interesting to note that small amounts of enol ethers from p-hydroxyphenyl units could be detected. Enol ether formation is much more conspicuous than during kraft pulping<sup>14</sup>, indicating the inability of sulfurfree alkaline processes to cleave the important phenolic  $\beta$ -0-4 linkages<sup>9</sup>.

### CONCLUSIONS

All the experimental data of second stage lignins according to the Organocell process point to sodalike degradation reactions. These data include extensive enol ether formation and a lower degree of demethylation and  $OH_{phen}$  formation (as compared with kraft pulping<sup>15</sup>). The reduced  $OH_{phen}$  formation is probably

TABLE 2

Main Degradation Products of Thioacidolysis ( $\mu\text{mol/g}$ )  
See also Fig. 3

	1S/40	2S/0	2S/20	2S/40
1 Coniferyl alcohol	126	34	29	25
2 Vanillic structure	50	55	45	59
3 Enol ether	41	130	166	179
4 Coniferyl aldehyde	51	5	-	-
5 Main degradation product*	656	573	422	404
6 Catechol	-	7	7	8

\* Noncondensed G-units with an intact  $\text{C}_3$ -side chain

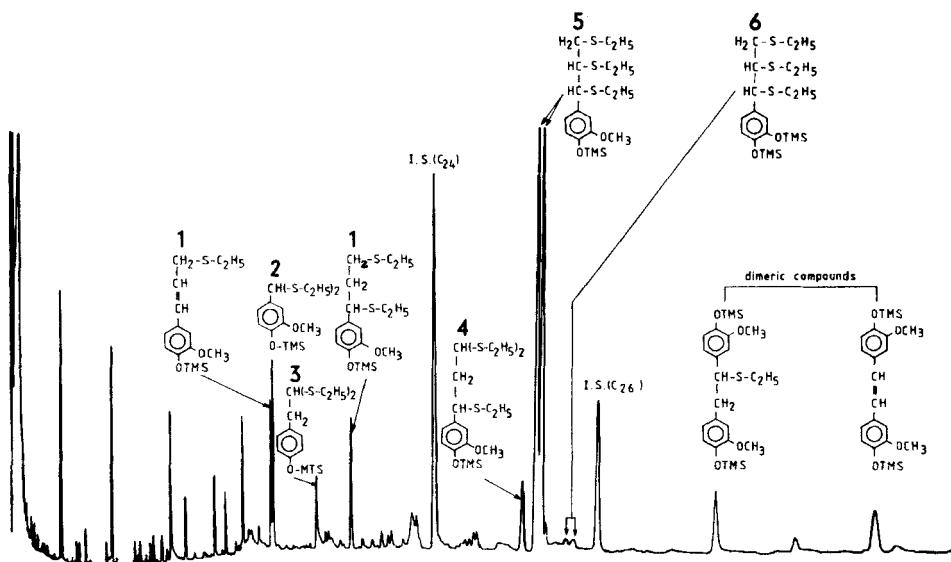


FIGURE 3: Gas chromatogram of thioacidolysis products of lignin 1S/40  
Structural units 1 - 6 are indicated

due to the lack of cleavage of phenolic  $\beta$ -0-4 linkages, which seems not to occur during Organocell pulping.

Active participation of methanol appears to be confined to a partial methylation of the  $\alpha$ -C-atom<sup>2</sup>, preventing quinone methide formation and, as a consequence, condensation reactions and also blocking the liberation of formaldehyde. Released formaldehyde prompts condensation reactions by means of diphenylmethane formation<sup>13</sup>. However, experimental data suggest that only every eighth to tenth phenylpropane unit is concerned. The superior efficiency of delignification during Organocell pulping of softwoods as compared to soda pulping could not as yet be definitely substantiated by the investigations of changes in lignin's structure.

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