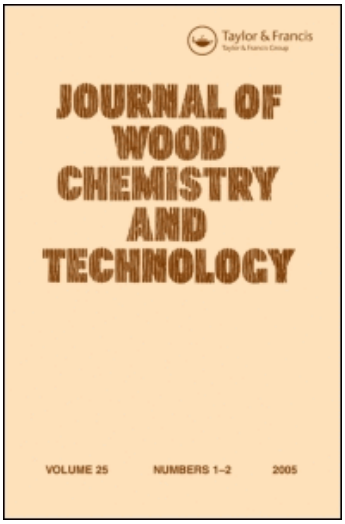


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# Characterization of Lignins from Organosolv Pulping According to the Organocell Process Part 1. Elemental Analysis, Nonlignin Portions and Functional Groups

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

## PART 1. ELEMENTAL ANALYSIS, NONLIGNIN PORTIONS AND FUNCTIONAL GROUPS

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## ABSTRACT

The Organocell process is the most advanced organosolv pulping process on a semi-technical scale. Delignification is performed by two-stage cooking involving methanol/water in the first stage with additional NaOH in the second stage. In this study spruce and pine lignins from the Organocell pilot plant and from laboratory cookings in a 20 l batch digester were characterized by means of elemental analysis, determination of nonlignin portions such as proteins, sugars and ash, and of functional groups (OH, CO, COOH, $OCH_3$). While first stage samples contained a considerable amount of impurities identified as organic nonlignin substances, second stage lignins showed characteristic changes in elemental composition and functional groups, except for the methoxyl groups, as reaction time progressed.

An accurate chemical characterization of these sulfurfree lignins is the essential prerequisite for their potential conversion into more valuable products.

## INTRODUCTION

Worldwide about 75 % of the chemical pulp are at present being produced by the kraft process. Despite the superior quality of kraft

pulps various problems such as environmental pollution, low pulp yields and high investment costs have stimulated the search for alternative pulping processes.

In the Federal Republic of Germany, where no kraft mills exist, chemical pulping is restricted to sulfite pulping, with calcium or magnesium as a base. Therefore, West Germany is currently in no position to produce pulps with kraftlike properties and thus completely dependent on kraft pulp imports. Sulfite pulping, having been on the decline for years, has generally attracted new interest with the development of new pulping techniques. With the addition of anthraquinone (AQ) softwoods can be transformed into high quality pulps by neutral or alkaline sulfite processes[1]. An interesting modification of alkaline sulfite pulping is the so-called ASAM (Alkaline Sulfite plus Anthraquinone and Methanol) process, which can cook all kinds of lignocellulosic raw materials down to low kappa numbers[2]. This process ist currently being transferred from laboratory to pilot plant scale in West Germany. Soda pulping in its various modifications, especially suitable for hardwoods and nonwood fibre materials[1] is the only established sulfurfree process so far. More recently Gasche[3] reported good results for softwoods by extending soda-AQ pulping with an additional oxygen stage.

Another approach to sulfurfree chemical pulping is organosolv pulping, i.e. using organic solvents as delignifying agents. In recent years research on organosolv pulping has been intensified yielding a variety of different pulping systems including alcohols, phenolic compounds, organic acids etc.[4,5,6,7].

Early interest has focused on alcohols and alcohol/water mixtures as delignifying agents according to the principal investigations by Kleinert[8,9]. The most advanced development on this basis is the Organocell process by Organocell GmbH in Munich[10,11]. In this two-stage process all wood species, including extractive-rich pine can be delignified by a methanol/water mixture (1:1) in the first

stage, whereas sodium hydroxide is added in the second stage. Pulps with almost kraft-like properties and kappa numbers as low as about 30 can be obtained. The process includes the recovery of sodium hydroxide and lignin by electrolysis[12]. After a thorough pilot plant operation period the Organocell process is now being tested in a continuously working 5 tons/day demonstration plant.

Whether the Organocell or any other new process is destined to gain ground in West Germany will depend, inter alia, on the following factors:

- the process should operate in relatively small production units
- the process should be suitable for all kinds of raw materials
- the process should meet extremely restrictive air and water regulations
- kraft-like strength properties and easy bleachability of the pulps are required
- the production of valuable and marketable by-products from polyoses and lignin should be possible.



The transformation of mainly sulfite and kraft lignins into potential new market products has been pursued in the past, yielding a variety of possibilities[13,14,15,16]. However, on account of mainly economic considerations the utilization of larger amounts of technical lignins for non-energy purposes has not become established practice so far.

Our study is aimed at a systematic investigation of semi-technical Organocell lignins and lignins obtained from 20 l batch cookings according to the Organocell process. The latter experiments serve a survey of the delignification course and the investigation of lignins from different cooking stages.

## EXPERIMENTAL

### Laboratory Lignins

These lignins were obtained by cooking spruce chips (Picea abies L. Karst.) in two stages in a 20 l batch digester equipped

with liquor circulation. In the first stage 2.2 kg of industrial size chips were heated to 170°C in 17 l of equal amounts of methanol and water. After reaching 170°C and a pressure of approx. 17 bar 300 ml of liquor were removed (stage 1/0). Further samples of 300 ml each were taken at 10 min intervals during the entire digestion period of 40 min for each stage.

In the second stage the chips were cooked in a methanol/water mixture (40:60) with addition of 30 % NaOH, based on dry wood. Reaction temperature and sampling method were identical to stage one while pressure reached only 16 bars. Samples from four cookings were combined and used as follows: By evaporating the methanol the first stage lignins were precipitated from the solution while the precipitation of the second stage lignins was accomplished by adding phosphoric acid, thus lowering the pH value to 4.0. The lignins were centrifuged, thoroughly washed with water and freeze dried.



## Pilot Plant Lignins

In contrast to laboratory conditions stage one cooking time in the pilot plant was only 20 min. The analyzed lignins were the following:

Spruce 1/P : spruce lignin, first stage/pilot plant
Spruce A/P : spruce lignin, second stage, precipitated with acid/pilot plant
Pine 1/P : pine lignin, first stage, pilot plant
Pine A/P : pine lignin, second stage, precipitated with acid/ pilot plant
Pine E/P : pine lignin, second stage, precipitated by electrolysis/ pilot plant

## Elemental Analysis

Elemental analysis was performed in an automatic analyzer (CHN-O-Rapid, Heraeus). The oxygen content was calculated by subtraction of the sum of carbon, hydrogen and nitrogen from 100 %.

## Sugar Analysis

After hydrolysis with trifluoroacetic acid[17] the sugars were determined in an automatic sugar analyzer (LC 2000, Biotronik).

## Titration of Carboxylic Groups and Phenolic OH Groups[18]

40 - 50 mg of lignin were dissolved in freshly distilled DMF. After addition of 10 mg of p-hydroxybenzoic acid as internal standard the solution was titrated potentiometrically with 0.05 n tetra-n-butylammonium hydroxide. To make sure that the COOH groups are quantitatively in the non-ionized state, the solution was adjusted previously to pH 1.5 with HCl. The glass electrode was prepared according to Pobiner[18].



## Content of Total OH Groups

The acetylated lignin samples were analyzed according to the procedure described by Mansson[19].

Conditions of the gas chromatograph (Fractovap 4160, Carlo Erba):
Temperature program: 5 min at 80°C, gradient to 130°C (5°C/min)
Injector temperature: 250°C
Detector temperature: 250°C (FID)
Column: OV 1

## Carbonyl Groups

The carbonyl groups were determined by hydrazone formation with pentafluorophenylhydrazine[20]. 100 mg of lignin were dissolved in aqueous acidic dioxane (dioxane/water/acetic acid = 9:1:1) and 100 mg of pentafluorophenylhydrazine were added. The mixture was kept under nitrogen for 10 days at 50°C. The hydrazone was then precipitated into ethyl ether. After washing three times with ethyl ether and once with petroleum benzene, the hydrazone was dried in vacuum over $P_2O_5$. The CO content was calculated according to the formula:

$$\% \text{ CO} = \frac{\% \text{ N}}{100 - 6.4286 \ \% \text{ N}} \times 100$$

Methoxyl Groups

The analyses were performed according to Viebock and Schwappach[21, 22].

Isolation of Milled Wood Lignin (MWL)

The procedure is described in detail elsewhere[23].

## RESULTS AND DISCUSSION

Table 1 presents the elemental composition of the investigated lignins. In the first stage there is a continuous increase in oxygen content with progressing reaction time. The extremely high values for carbon and particularly hydrogen at the beginning of stage 1 can be considered a first indication of the presence of high amounts of nonlignin substances other than proteins, sugars and ash in the precipitate. Washing with water did not remove these components which account for almost 50 % of the precipitate at the onset of digestion ( time 0), but drop rapidly to about 10 % after 40 min. They cannot be attributed to degradation products such as acetic or lactic acids which would have been removed during the washing at the latest, but are probably extractive compounds and sugar degradation products. This view finds further support when examining the content of the methoxyl groups. Since in the early phase of stage 1 no noticeable cleavage of methoxyl groups appears probable, the low $OCH_3$ values for the first 3 samples must be attributed to the lignin accompanying impurities mentioned above. Therefore the $C_9$-formulae of the early first-stage lignins were not calculated and all the functional groups of the stage 1 lignins are expressed in percent rather than as functional group per $C_9$ unit. The presence of nonlignin portions was also reported by Chua and Wayman[24] in their investigation of autohydrolysis aspen lignins. These authors postulated the incorporation of hemicellulose degradation products into the lignin during autohydrolysis.

TABLE 1

Elemental Composition, Methoxyl Content, $C_9$-Formulae and $C_9$-Molecular Weight of Lignins.

(Values are corrected for proteins, sugars and ash)

| Lignin | C (%) | H (%) | O (%) | $OCH_3$ (%) | $C_9$-formulae | Molecular weight |
|---|---|---|---|---|---|---|
| Stage 1/ 0 | 68.52 | 7.30 | 24.18 | 9.50 | - | - |
| Stage 1/10 | 67.74 | 6.88 | 25.38 | 12.24 | - | - |
| Stage 1/20 | 67.15 | 6.77 | 26.08 | 13.77 | - | - |
| Stage 1/30 | 66.89 | 6.60 | 26.51 | 14.35 | $C_9H_{9.07}O_{2.10}(OCH_3)_{0.82}$ | 176.23 |
| Stage 1/40 | 66.80 | 6.51 | 26.69 | 14.95 | $C_9H_{8.89}O_{2.10}(OCH_3)_{0.85}$ | 177.16 |
| Stage 2/ 0 | 65.49 | 5.95 | 28.56 | 15.76 | $C_9H_{7.98}O_{2.32}(OCH_3)_{0.92}$ | 182.00 |
| Stage 2/10 | 65.53 | 6.02 | 28.45 | 15.99 | $C_9H_{8.05}O_{2.30}(OCH_3)_{0.94}$ | 182.15 |
| Stage 2/20 | 65.94 | 5.97 | 28.09 | 15.93 | $C_9H_{7.92}O_{2.24}(OCH_3)_{0.93}$ | 180.83 |
| Stage 2/30 | 65.69 | 5.95 | 28.36 | 15.74 | $C_9H_{7.94}O_{2.29}(OCH_3)_{0.92}$ | 181.37 |
| Stage 2/40 | 64.14 | 5.91 | 29.95 | 15.67 | $C_9H_{8.09}O_{2.54}(OCH_3)_{0.94}$ | 186.13 |
| Spruce 1/P | 69.23 | 6.45 | 24.32 | 11.85 | - | - |
| Spruce A/P | 67.05 | 5.95 | 27.00 | 15.87 | $C_9H_{7.74}O_{2.09}(OCH_3)_{0.91}$ | 177.47 |
| Pine 1/P | 66.97 | 6.31 | 26.72 | 15.00 | $C_9H_{8.51}O_{2.10}(OCH_3)_{0.85}$ | 176.73 |
| Pine A/P | 67.03 | 5.75 | 27.22 | 15.76 | $C_9H_{7.42}O_{2.12}(OCH_3)_{0.90}$ | 177.40 |
| Pine E/P | 66.24 | 5.76 | 28.00 | 15.78 | $C_9H_{7.51}O_{2.22}(OCH_3)_{0.92}$ | 179.77 |
| Spruce MWL | 62.99 | 5.72 | 31.29 | 15.34 | $C_9H_{7.93}O_{2.76}(OCH_3)_{0.94}$ | 189.46 |

In the second stage the situation is more complex. The oxygen content drops to a minimum of 28.1 % after 20 min, then rises rapidly to almost 30 % towards the end of digestion (Fig.1).The methoxyl content remains constant at about 0.93 $OCH_3/C_9$ unit. As Nakano[25] had demonstrated the methylation of benzylalcoholic hydroxyl groups of lignin model substances with a free phenolic OH group in methanol/water systems, an increase in methoxyl content during the second stage was expected. And, indeed, a partial methylation of the $\alpha$-C-OH

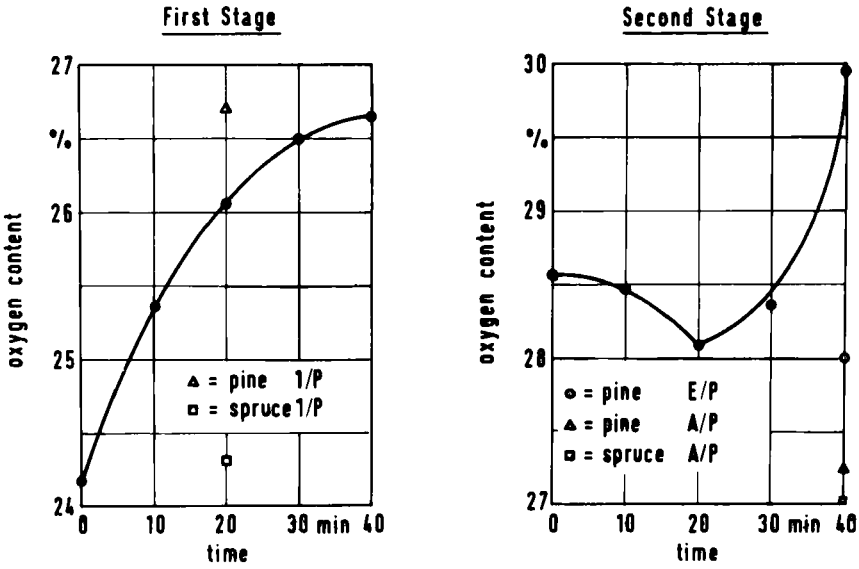


FIGURE 1: Oxygen contents of the laboratory and pilot plant lignins.

group can be deduced from $^{1}$H-NMR spectra. However, the chemical analyses demonstrate that the formation of new methoxyl groups during organosolv pulping according to the Organocell process should be rather low. The lower oxygen contents for the second stage pilot plant lignins indicate a somewhat higher degree of condensation in comparison with the laboratory lignins. However, an interpretation of the pilot plant lignins is as yet ambiguous inasmuch as they are merely single random samples with partly uncertain cooking conditions.

Apart from the nonlignin portions mentioned above, the lignins contained further impurities such as proteins, sugars and ash. Tables 2 and 3 present corresponding data.

TABLE 2

Nitrogen, Protein and Ash contents of the Laboratory Lignins (Protein = 6.25 x N).

| | First Stage | | | Second Stage | | |
|---|---|---|---|---|---|---|
| Time min | N % | Protein % | Ash % | N % | Protein % | Ash % |
| 0 | 0.35 | 2.2 | - | - | - | 8.6 |
| 10 | 0.33 | 2.1 | - | - | - | 8.4 |
| 20 | 0.22 | 1.4 | 0.1 | - | - | 15.2 |
| 30 | 0.20 | 1.3 | - | - | - | 17.9 |
| 40 | 0.20 | 1.3 | - | - | - | 16.3 |



TABLE 3

Nitrogen, Protein and Ash Contents of the Pilot Plant Lignins (Protein = 6.25 x N).

| Lignin | | N % | Protein % | Ash % |
|---|---|---|---|---|
| Spruce | 1/P | 0.30 | 1.9 | 0.1 |
| Spruce | A/P | 0.24 | 1.5 | 0.9 |
| Pine | 1/P | 0.36 | 2.2 | 0.1 |
| Pine | A/P | 0.19 | 1.2 | 10.8 |
| Pine | E/P | - | - | 7.4 |

With the exception of pine A/P and spruce A/P lignins the proteins are exclusively confined to the first stage. The high ash contents found in the second stage are mainly due to residual NaOH and $H_3PO_4$.

The polysaccharide composition and portions are listed in Tables 4 and 5.

TABLE 4

Sugar Contents of the Laboratory Lignins.

| Sugar | | First Stage 0 | 10 | 20 min. | 30 | 40 | Second Stage 0 | 10 | 20 min. | 30 | 40 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Rhamnose, | % | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | - | - | - | - | 0.01 |
| Mannose, | % | 0.43 | 0.37 | 0.33 | 0.43 | 0.32 | 0.13 | 0.17 | 0.18 | 0.20 | 0.21 |
| Arabinose, | % | 0.16 | 0.17 | 0.14 | 0.16 | 0.21 | 0.08 | 0.09 | 0.10 | 0.10 | 0.10 |
| Galactose, | % | 0.23 | 0.22 | 0.19 | 0.23 | 0.17 | 0.23 | 0.31 | 0.39 | 0.46 | 0.49 |
| Xylose, | % | 0.06 | 0.07 | 0.07 | 0.11 | 0.08 | 0.35 | 0.47 | 0.78 | 0.60 | 0.63 |
| Glucose, | % | 0.79 | 0.60 | 0.50 | 0.50 | 0.30 | 0.15 | 0.09 | 0.10 | 0.16 | 0.12 |
| Total sugars, | % | 1.69 | 1.46 | 1.24 | 1.45 | 0.99 | 0.92 | 1.15 | 1.58 | 1.51 | 1.56 |
| " polysacch. | % | 1.51 | 1.31 | 1.11 | 1.30 | 0.89 | 0.82 | 1.02 | 1.41 | 1.35 | 1.39 |

TABLE 5

Sugar Contents of the Pilot Plant Lignins and Spruce MWL.

| Sugar | | Spruce 1/P | Spruce A/P | Pine 1/P | Pine A/P | Pine E/P | Spruce MWL |
|---|---|---|---|---|---|---|---|
| Rhamnose, | % | - | 0.01 | 0.01 | - | - | - |
| Mannose, | % | 0.26 | 0.36 | 0.88 | 0.31 | 0.28 | 0.74 |
| Arabinose, | % | 0.07 | 0.09 | 0.10 | 0.12 | 0.15 | 0.13 |
| Galactose, | % | 0.16 | 0.48 | 0.42 | 0.58 | 0.53 | 0.14 |
| Xylose, | % | 0.12 | 0.50 | 0.30 | 0.50 | 0.42 | 0.37 |
| Glucose, | % | 0.28 | 0.21 | 0.50 | 0.21 | 0.16 | 0.77 |
| Total sugars, | % | 0.95 | 1.66 | 2.21 | 1.73 | 1.55 | 2.15 |
| " polysacch. | % | 0.84 | 1.54 | 1.98 | 1.55 | 1.39 | 1.93 |

Except for lignin pine 1/P all samples have lower sugar contents than spruce MWL. The individual sugar compositions of first stage lignins resemble that of spruce MWL, while in second stage lignins low amounts of glucose, a remarkable increase in xylose and, to a lesser extent, also in mannose and galactose were observed. These data suggest that xylans and also galactoglucamannans are predominantly affected in the second half of stage 2.

TABLE 6

Total and Phenolic OH, Carboxylic and Carbonyl Groups of MWL Laboratory and Pilot Plant Lignins.

| Lignin | Total OH | | Phenolic OH | | COOH | | CO | |
|---|---|---|---|---|---|---|---|---|
| | % | per $C_9$ | % | per $C_9$ | % | per $C_9$ | % | per $C_9$ |
| Stage 1/ 0 | 7.39 | - | 1.94 | - | 6.06 | - | 2.29 | - |
| Stage 1/10 | 9.14 | - | 2.56 | - | 5.19 | - | 2.45 | - |
| Stage 1/20 | 9.49 | - | 2.83 | - | 4.36 | - | 1.82 | - |
| Stage 1/30 | 9.34 | 0.97 | 3.17 | 0.33 | 4.27 | 0.17 | 1.81 | 0.11 |
| Stage 1/40 | 9.46 | 0.99 | 3.13 | 0.33 | 3.94 | 0.16 | 1.41 | 0.09 |
| Stage 2/ 0 | 11.26 | 1.21 | 2.92 | 0.31 | 5.17 | 0.21 | 1.15 | 0.07 |
| Stage 2/10 | 11.10 | 1.19 | 2.93 | 0.31 | 4.54 | 0.18 | 1.07 | 0.07 |
| Stage 2/20 | 10.15 | 1.08 | 2.68 | 0.29 | 4.21 | 0.17 | 0.91 | 0.06 |
| Stage 2/30 | 11.31 | 1.21 | 2.95 | 0.31 | 4.73 | 0.19 | 0.91 | 0.06 |
| Stage 2/40 | 11.47 | 1.26 | 3.02 | 0.33 | 5.57 | 0.23 | 1.04 | 0.07 |
| Spruce 1/P | 10.08 | - | 3.44 | - | 4.95 | - | 2.13 | - |
| Spruce A/P | 11.20 | 1.17 | 3.22 | 0.34 | 5.36 | 0.21 | 1.43 | 0.09 |
| Pine 1/P | 9.99 | 1.04 | 2.97 | 0.31 | 4.34 | 0.17 | 1.85 | 0.12 |
| Pine A/P | 9.55 | 1.00 | 2.80 | 0.29 | 5.79 | 0.23 | 1.83 | 0.12 |
| Pine E/P | 9.63 | 1.02 | 2.43 | 0.26 | 6.27 | 0.25 | 2.12 | 0.14 |
| Spruce MWL | 10.31 | 1.15 | 1.61 | 0.18 | 1.55 | 0.06 | 2.63 | 0.18 |



The results of OH, CO and COOH determinations are summarized in Table 6.

The COOH groups and the phenolic OH groups were quantified by a simultaneous titration of weak (COOH) and very weak (phenolic OH) acids. Applying this method, Scalbert and Monties[26] concluded that some of the phenolic OH groups were "hyperacidic" and titrated with the COOH groups as a consequence. To find out whether this phenomenon influences the analysis of the organosolv lignin, the phenolic OH groups of three pilot plant lignins were also analyzed by the UV differential spectroscopy method[27]. Table 7 reveals that the potentiometric titration yields almost the same results as the UV method. If part of the phenolic OH groups are titrated as COOH groups the potentiometric titration would give lower values. Furthermore

TABLE 7

Comparison of UV Differential Spectroscopy and Titration of Phenolic OH Groups

| Lignin | UV Method Phenolic OH % | Titration % |
|---|---|---|
| Pine 1/P | 3.01 | 2.97 |
| Pine A/P | 2.69 | 2.80 |
| Pine E/P | 2.42 | 2.43 |



the content of COOH groups obtained by titrating spruce MWL (0.06/$C_9$) proved to be almost identical to results published by Marton[28] (0.05/$C_9$) who had used the methylation method.

Another source of error may be uronic acids from degraded carbohydrates, which would be titrated together with the weak acids. Although uronic acids were not detected by sugar analysis, traces might interfere with the COOH groups determination.

The decrease in COOH content during the first 20 min of the second stage (Fig. 2) is presumably due to reasons of solubility. Part of the carboxylic groups may be formed in the first stage already and become soluble due to the ionization effect under the alkaline conditions of the second stage.

As a consequence COOH groups are preferably being solubilized at the beginning of stage 2 which explains the high contents at 0 and 10 min. The generation of new carboxylic groups is responsible for the distinct increase in the second half of stage 2. The results of the first three samples of stage 1 are again strongly in-

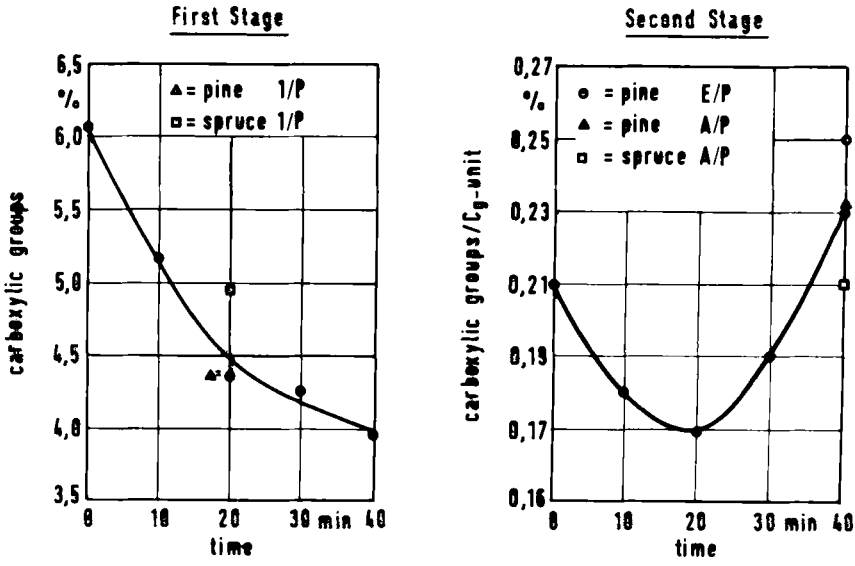


FIGURE 2: Carboxylic groups of the laboratory and pilot plant lignins.



fluenced by nonlignin portions. The electrolytically precipitated sample (pine E/P) shows an extremely high COOH content, but many more samples of this type will have to be investigated to understand the influence of electrolysis on the chemical composition of these organosolv lignins.

The frequency of phenolic OH groups occurrence can give information on the degree of ether cleavages and, in combination with molecular weight determination, comparative deductions on the degree of condensation are possible. Softwood MWL has thoroughly been investigated for its phenolic OH content, ranging between 0.16 and 0.30 groups/$C_9$[28, 29]. Spruce MWL from this study yielded 0.18 groups/$C_9$. Figure 3 shows both the phenolic and total hydroxyl contents. The similar courses of the graphs in both stages is striking. In the second stage there is again a minimum at 20 min, as for the oxygen

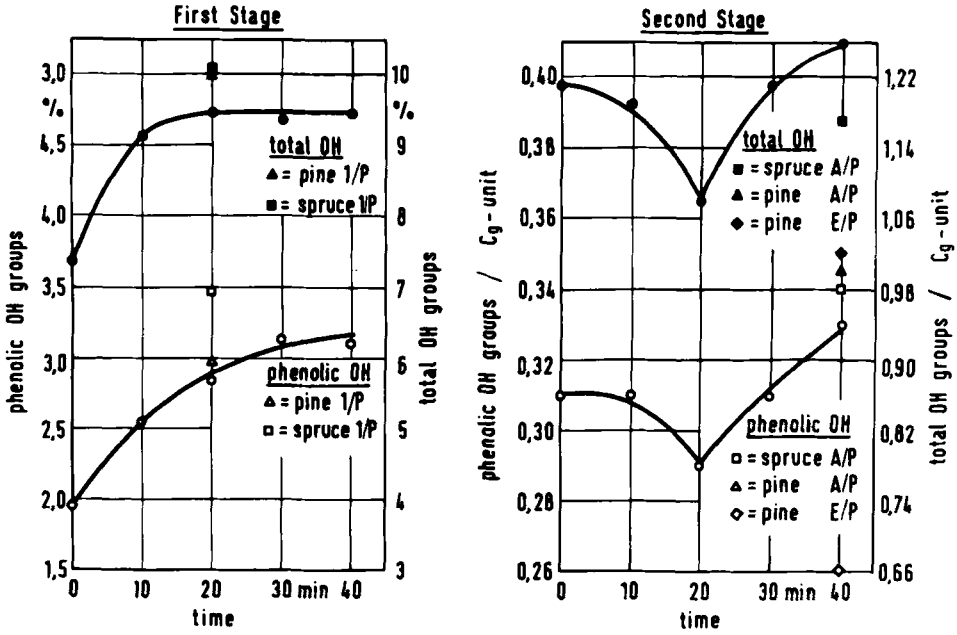


FIGURE 3: Phenolic and total OH groups of the laboratory and pilot plant lignins.



content. Reasons of solubility can be held responsible for the decrease within the first 20 min. Also, the molecular size of the lignins influences the number of OH groups. With other parameters remaining constant, smaller lignin molecules will inevitably yield higher amounts of OH groups. Preliminary investigations on the molecular weight distribution indicate that the highest molecular weights are found at 10 and 20 min. In the second half of stage 2 an intensified cleavage of ether bonds diminishes the molecular weights and raises the OH contents. An interpretation of the first stage results is very difficult but the steep increase in the number of OH groups during the first 20 min is certainly due to the nonlignin portions.

On the whole the pilot plant lignins in this study do not differ much from the laboratory lignins. The slightly lower content of aliphatic OH groups (calculated by subtraction of phenolic from total OH) indicate a higher degree of side chain degradation.

The most extensively used determination of the CO content is oximation with hydroxylamine hydrochloride and subsequent titration of the released HCl[28].

Low reaction speed and a weakly acidic pH required for a quantitative reaction are, however, the serious drawbacks in this reaction type. The acidic pH, in particular, gives solubility problems with the pilot plant lignins. The reduction method with $KBH_4$[30] causes no solubility problems but may yield uncharacteristically high values[31]. As we finally managed to dissolve all Organocell lignins by applying ultrasonics in a weakly acidic dioxane/water mixture (dioxane/water/acetic acid = 9:1:1) the CO determination via hydrazone formation with pentafluorophenylhydrazine (PFPH) was feasible[20]. Studies on model compounds, including phenylpropane-1,2-dione as a slowly reacting α,β-diketone were successful, and spruce MWL yielded 0.20 CO groups/$OCH_3$, a value also reported by Marton et al.[31]. The CO values in Table 6 make it obvious that the first stage laboratory lignins and the pilot plant lignins have comparable CO contents whereas the second stage laboratory lignins yielded considerably lower CO values.

The minimum values of all functional groups of the second stage at 20 min correspond to the low oxygen contents of corresponding lignins at 20 min due to the considerable amount of oxygen in these functional groups.

## CONCLUSIONS

Apart from noticeable differences in carbonyl contents in the second stage the chemical composition of the pilot plant lignins is similar to that of the laboratory samples.

- First stage lignins contain a considerable amount of impurities due to organic ingredients, particularly at the beginning of the digestion process.
- The carbohydrate portions of all investigated samples are remarkably low.
- With the exception of the methoxyl groups the functional groups of the second stage exhibit similar concentration patterns, with a minimum at 20 min.
- In the second stage methylation of the $\alpha$C-OH group is negligible, as can be deduced from the constant methoxyl values. However, methylation does occur to some extent in the first stage.
- For a better understanding of the Organocell process further research including investigations of the residual lignin and the use of additional techniques such as spectroscopic methods, the analysis of oxidative degradation products and the determination of the molecular weight distribution is required. The results will be reported in the subsequent parts of this series.



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