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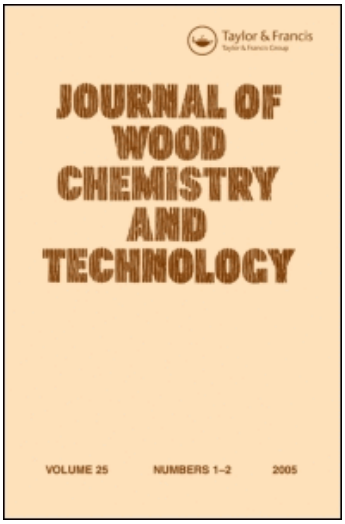

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Characterization of Lignins from Organosolv Pulping According to the Organocell Process. Part 3. Permanganate Oxidation and Thioacidolysis

Albert Lindner[a]; Gerd Wegener[a]
[a] Institute for Wood Research University of Munich, Munich 40, Federal Republic of Germany

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CHARACTERIZATION OF LIGNINS FROM ORGANOSOLV PULPING ACCORDING TO THE ORGANOCELL PROCESS

PART 3. MOLECULAR WEIGHT DETERMINATION AND INVESTIGATION OF FRACTIONS ISOLATED BY GPC

Albert Lindner and Gerd Wegener
Institute for Wood Research
University of Munich
Winzererstrasse 45, D-8000 Munich 40
Federal Republic of Germany

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ABSTRACT

Both residual lignins and lignins isolated from the pulping liquor of 20 l batch cookings of spruce chips according to the Organocell process were subjected to HPSEC. Checking the resulting M_n-values by vapor pressure osmometry confirmed the HPSEC data except for first stage lignins with short cooking times, where the different elution behavior caused by high portions of organic nonlignin substances is held responsible for these discrepancies.

The molecular weights of residual lignins, which were found to be considerably higher than those of the corresponding soluble lignins, are dependent on yields and/or isolation procedure and are therefore not representative of the total lignin in the pulp.

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The investigation of lignin fractions isolated according to molecular weight by GPC reveals the preferential side chain degradation of the low molecular weight portions, which is explained by the protection of high molecular weight particles within association complexes and/or by specific reactions of structural units, which are typical for low molecular weight lignins.

INTRODUCTION

The preceding parts of this series discussed the analytical data of lignins originating from the pulping liquors and cooking residues of Organocell pulping[1,2]. The analyses included elemental composition and determination of nonlignin portions and functional groups which were found to display characteristic concentration patterns in relation to cooking time. In order to find out to what extent the cooking time affects the molecular weights of both soluble and residual lignins, the lignins described in parts 1 and 2 were subjected to molecular weight determination by means of high performance size exclusion chromatography (HPSEC) and vapor pressure osmometry (VPO).

HPSEC has become a widely used technique for determining molecular weight distributions (MWD) of lignins[3-5]. For routine investigations column calibration is usually performed with polystyrene standards, the suitability of which however is open to question: Sarkanen et al.[6] found that calibrating a Sephadex G 100/0.1 n NaOH column system with paucidisperse kraft lignin fractions causes a parallel shift of a calibration curve originally set with

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sulfonated polystyrene standards. In the subsequent MWD-analysis M_w-values turned out to be 1.7 times higher than those obtained by using polystyrene calibration. Optimization of column calibration by applying paucidisperse lignin fractions with molecular weights determined by ultracentrifugation or light scattering has also been reported by other authors[7,8]; however, these papers do not include comparisons with conventional calibration techniques.

Interactions between different lignin molecules may be another source of error, which can be reduced if not completely eliminated by carefully choosing the experimental parameters: By adding LiCl to the eluent (DMF) Connors et al.[9] were able to suppress lignin associations in Sephadex LH 60 and Octylsepharose CL-4B columns and finally obtained unimodal elution curves. Sarkanen et al.[10] stated that the extent of lignin association is strongly influenced by the isolation procedure. To obtain maximum dissociation the lignin had to be kept in solution for up to 1700 h (0.5 g lignin per liter 0.1 n NaOH).

In their thorough investigation of HPSEC systems for MWD determination of lignins, Chum et al.[11] found styrene/divinylbenzene columns with THF as eluent to be a suitable means for the analysis of acetylated lignins. Igepal and polystyrene standards were used for column calibration. In order to find out whether this HPSEC system can also be applied for lignins from Organocell pulping, the M_n-values calculated from the elution curves were checked by VPO measurements.

The other aspect of this paper concerns lignin's heterogeneity as evidenced by the characterization of

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fractions of a second stage Organocell lignin separated on a GPC column according to molecular weight. Interest in this type of investigation was twofold: Chemical and physical variations between different molecular weight fractions may play an important role in the utilization of lignin for non-energy purposes, as can be seen by high molecular weight lignosulfonates being more suitable for the substitution of phenol/formaldehyde resins for particleboards[12,13] or by the superior dispersing activity of low molecular weight lignosulfonates and alkali lignins[14]. Besides, we hoped to gain some insight into the solution behavior of these lignins. Garver and Sarkanen[15] described kraft lignin association complexes with preferential interactions between lower and higher molecular weight particles which appeared to be stoichiometrically constrained. Due to this supramolecular arrangement, high molecular weight particles are considered incorporated within the complexes and thus shielded from chemical degradation during delignification. As association complexes of Organocell lignin solutions have been observed for some time and have quite recently been confirmed by light scattering measurements, the chemical characterization of lignin fractions appeared to be a promising way of gaining more information about the properties of these complexes.

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EXPERIMENTAL

Origin of the lignins

The Organocell process was simulated in a 20 l batch digester with liquor circulation[1]. 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 isolation of the soluble lignins is described elsewere[1]. Residual lignins were isolated as milled wood lignins, second stage samples were alternatively liberated by enzymatic treatment[2].

Nomenclature:

The denomination of the cooking stage (1S or 2S) is followed by the cooking time expressed in minutes. Suffix 'R' stands for residual lignins isolated via ball-milling, while enzymatically liberated lignins are marked with 'RE'. Examples:

1S/10: soluble lignin, first stage, 10 min.
2S/20 R: residual lignin, second stage, 20 min. isolated via ball-milling
2S/20 RE: residual lignin, second stage, 40 min. enzymatically liberated.

Additionally the following lignins from the Organocell pilot plant were analyzed[1]:

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

The lignin used for fractionation (2S/DA 1) originates from the 5 tons/day demonstration plant used by Organocell, Munich, West Germany[16], and was isolated by acid precipitation (H_3PO_4).

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Molecular Weight Determination

Vapor Pressure Osmometry:

M_n-values were determined in a vapor pressure osmometer (No. 11.00, Knauer). First stage samples and residual lignins were measured in DMF solutions at 90°C, second stage samples in both DMF (90°C) and THF (45°C). Benzil and curcumin were used for calibration. Chloroform solutions were used for the acetylated samples.

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HPSEC:

For HPSEC analysis the lignins were acetylated according to Gierer and Lindeberg[17]. Styrene/divinylbenzene copolymer gels were used for the experiments. Four Hibar columns (LiChrogel PS 4000/ PS 400/ PS 40/ PS 1, Merck) were connected in series. Column calibration was performed with polystyrene standards (Waters) in the 35000 - 2350 range. For the low molecular weight range curcumin (Roth) and vanillin (Merck) were added. The following conditions applied:

sample concentration	4 mg/ml
solvent	THF
temperature	45°C
flow rate	1 ml/min
sample loading	20 µl

UV detection was performed at 280 nm (photometer No. 731.8700000, Knauer). Quantitative calculations involved the program GPC Enhancement for Chromatochart (Interactive Microware, Inc.).

Preparative Fractionation of 2S/DA 1

Lignin fractionation was performed with a Sephadex G 75/0.1 n NaOH system:

column dimensions: 2.4 x 130 cm

lignin quantity: 0.5 g of 165 g per liter 0.1 n NaOH

14 fractions (F 1 - F 14) were collected, precipitated by lowering the pH to 2.0 with 1.5 n HCl, centrifuged, washed several times with water and freeze dried. Fractions F2, F 3, F 4, F 6, F 8, F 10 (and F 12) were used for further investigations.

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Analytical Data of the Lignin Fractions

Elemental composition and sugar analysis were previously described. Functional groups were estimated from ^{1}H-NMR-spectra, recorded on a 270 MHz instrument (JNM-GX 270, Jeol)[18].

RESULTS AND DISCUSSION

Tables 1 - 3 list the M_n-values of both HPSEC and VPO. Samples of the same stage (e.g. 2S/20 and 2S/40) were analyzed within this systematic study. A detailed interpretation, however, is restricted due to the similarity of the respective samples. Apart from first stage samples with short cooking times (0 - 20 min) the values correlate reasonably well. In order to find out whether the considerable discrepancies of those first stage samples are due to undesired chemical reactions during acetylation, an acetylated sample (1S/0) was subjected to VPO. A M_n-value of 740

TABLE 1

M_n of Spruce Lignins from 20 l Batch Cookings

M_n	1S/0	1S/10	1S/20	1S/30	1S/40	2S/0	2S/10	2S/20	2S/30	2S/40
HPSEC*	1080	903	950	780	720	1500	1590	1480	1490	1210
VPO	630	630	730	730	630	1360	1600	1350	1750	1400

*values are corrected for acetyl groups

TABLE 2

M_n of Pilot Plant Lignins[1]:

M_n	Spruce 1/P	Spruce A/P	Pine 1/P	Pine A/P
HPSEC*	1135	1146	1704	2456
VPO	630	850	860	2200

*values are corrected for acetyl groups

TABLE 3

M_n of Fractions from 2S/DA 1

M_n	F 6	F 8	F 12
HPSEC	2670	1600	1200
VPO**	3170	1400	1020

**acetylated fractions were used

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(corrected for acetyl groups) indicates that other reasons are responsible for these differences. Obviously, the high portions of nonlignin substances found in first stage samples with short cooking times cause a different elution behavior and thus pretend to have unusually high M_n-values[1]. It is interesting to note that this phenomenon is also encountered with the GPC system Sephadex G 75/0.1 n NaOH, where the elution curve of 1S/0 also suggests higher molecular weights than the one of 1S/40 (Figure 1).

Provided, however, that the samples are reasonably pure, the M_n-values of the HPSEC analyses may be considered satisfactory. This does not necessarily imply a correct calibration curve over the whole molecular weight range defined by the standards. M_n-values are average values, where the small portions of high molecular weight molecules encountered in lignins according to the Organocell process add only very little to M_n. However, a correct calibration for the greater part of the molecular weight range in question may be assumed. At present the high molecular weight range is being checked by experiments involving light scattering.

Another problem is posed by the mathematical correction of the acetyl groups, which assumes a constant total OH content over the entire molecular weight range. Considering the immense diversity concerning the functional group composition of different molecular weight fractions (see below), such an assumption seems questionable at first sight. Table 7 shows, however, that despite enormous variations of aliphatic and phenolic OH contents the total OH content used for the correction remains remarkably con-

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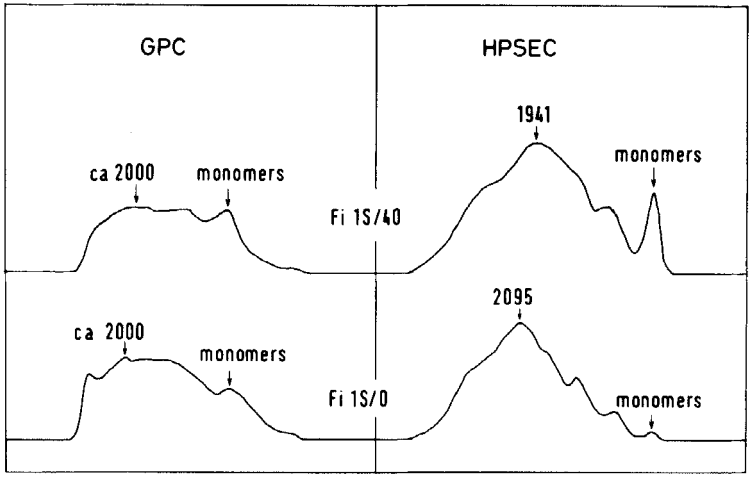

FIGURE 1: Comparison of GPC and HPSEC of two first stage lignins

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stant in all investigated fractions so that the error caused by the mathematical correction should be tolerable.

Another potential source of error encountered during UV-detection and with its origin in absorption coefficients which vary with molecular weight, was not pursued in this investigation. Lange et al.[19] reported, however, that varying absorption coefficients cause aberrations of 5 % at the utmost.

Figure 1 depicts the elution curves of two first stage samples recorded from runs on a GPC column (Sephadex G 75/0.1 n NaOH) calibrated with sulfonated polystyrenes and on our HPSEC system. Although the elution profiles differ markedly from each other on account of differences concerning exclusion limits and graduation of the x-axis, both systems indicate peak

TABLE 4

Molecular Weight Distribution (MWD) of Spruce Lignins from 20 l Batch Cookings

Range	1S/0	1S/10	1S/20	1S/30	1S/40	2S/0	2S/10	2S/20	2S/30	2S/40
>30000	0.00	0.37	0.00	0.11	0.11	1.05	1.88	2.02	1.87	1.09
30000 - 20000	0.47	1.04	0.88	0.66	0.67	2.89	3.56	3.31	3.36	2.53
20000 - 10000	4.03	4.68	6.25	5.24	5.95	13.28	13.30	12.21	12.82	11.03
10000 - 7500	5.17	5.23	6.17	5.35	5.65	8.63	8.34	7.72	8.07	7.63
7500 - 5000	11.18	11.10	11.48	10.14	9.83	12.14	11.85	11.08	11.57	12.19
5000 - 4000	7.26	6.42	6.37	6.25	6.10	6.74	5.98	5.63	5.74	6.13
4000 - 3000	10.75	10.06	9.97	9.00	9.02	9.02	9.06	8.48	8.58	8.02
3000 - 2000	16.56	14.35	15.38	14.51	14.12	13.55	13.59	13.28	13.28	12.32
2000 - 1500	9.69	9.81	10.54	9.13	8.80	8.73	8.64	8.90	8.73	8.96
1500 - 1000	11.93	11.90	10.07	11.63	11.80	10.04	9.96	10.87	10.48	10.89
1000 - 750	5.63	6.36	5.53	6.45	5.91	5.01	5.52	6.52	6.03	6.03
750 - 500	8.07	7.43	6.69	7.03	7.53	4.75	5.13	6.02	5.66	6.78
500 - 300	5.19	5.01	4.67	5.96	5.02	3.52	3.17	3.96	3.80	4.79
< 300	4.07	6.23	5.98	8.55	9.49	0.65	0.00	0.00	0.00	1.60
M_w	3270	3566	3693	3333	3421	5684	6186	5951	6008	5199
M_n	1235	1107	1171	961	964	1918	2029	1848	1910	1555
M_w (corrected)	2765	2909	2992	2708	2773	4447	4855	4758	4696	4051
M_n (corrected)	1044	903	949	781	781	1501	1592	1478	1493	1212
M_w/M_n	2.65	3.22	3.15	3.47	3.55	2.96	3.05	3.22	3.15	3.34
Peak maximum	2095	1821	2153	1861	1941	1940	1790	1824	1783	1403

maxima of about 2000 and the existence of monomers with increasing proportions from 1S/0 to 1S/40. The reproducibility of these data on different systems is an important factor in assessing the HPSEC system, all the more as the Sephadex G 75/0.1 n NaOH system is considered reliable for the molecular weight determination of lignins[20]. The quantitative evaluations of the HPSEC runs are listed in Table 4 which can be summarized as follows:

- Samples from the same cooking stage exhibit very similar elution curves.
- First stage lignins are characterized by high portions of monomers (<300), especially at the end of stage 1.
- Only traces of monomers could be detected in second stage samples. Although the absence of strongly nucleophilic agents such as SH^- ions

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prevents the cleavage of phenolic ß-0-4 bonds and, as a consequence, the formation of considerable amounts of monomers, these structures should nevertheless be traceable in second stage lignins. Presumably, these reaction products are quickly removed by condensation reactions involving quinone methide intermediates[21].

- Low molecular weight portions (<750) increase towards the end of stage 2 (2S/40). This is the only sample with a monomer fraction above 1 %.
- In spite of lower M_w- and M_n-values the peak maxima of first stage lignins are composed of higher molecular weight molecules than the second stage lignins.

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As expected residual lignins are composed of much higher molecular weight particles. With the exception of 2S/40 R the elution profiles are rather uniform, differences between the two cooking stages are clearly reduced as compared to soluble lignins (Table 5, Figure 2).

While the elution curves of 2S/20 (R + RE) correlate closely, the isolation method has a much stronger impact on 2S/40 (R + RE), generating low yields and a narrow MWD in the medium molecular weight range for the ball-milled sample (2S/40 R). The obvious interdependence between MWD and yields[2] clearly demonstrates that the MWDs of isolated residual lignins are by no means representative of the total lignin in the pulp in terms of absolute evaluations so that the interpretation must be restricted to relative assignments.

TABLE 5

MWD of Residual Lignins from 20 l Batch Cookings

Range	MWL	1S/20R	1S/40R	2S/20R	2S/40R	2S/20RE	2S/40RE
>30000	2.33	3.47	1.64	10.05	0.00	7.51	8.12
30000 - 20000	5.05	7.19	5.31	9.29	0.64	7.47	8.18
20000 - 10000	19.20	30.04	27.17	23.63	9.06	21.81	21.39
10000 - 7500	14.44	16.52	16.78	11.49	10.10	11.05	10.25
7500 - 5000	13.84	16.72	16.98	12.24	20.45	13.02	12.62
5000 - 4000	7.72	6.40	7.37	5.16	12.11	5.73	5.35
4000 - 3000	8.74	6.62	7.96	6.69	15.88	7.15	6.17
3000 - 2000	11.56	6.86	8.26	7.87	18.79	8.64	8.04
2000 - 1500	6.09	2.49	3.05	4.10	6.22	4.60	4.63
1500 - 1000	5.20	1.79	2.42	4.49	3.66	5.57	4.89
1000 - 750	2.31	0.60	0.94	2.07	1.04	2.75	2.65
750 - 500	2.00	0.41	0.92	1.91	0.93	2.57	2.69
500 - 300	1.52	0.44	0.62	0.92	0.13	1.79	4.39
<300	0.00	0.44	0.59	0.11	0.00	0.34	0.63
M_w	7912	10435	8934	13134	5230	11167	11416
M_n	3087	4807	4013	3820	3349	3042	2605
M_w (corrected)	6306	8233	7042	10296	4224	8735	8885
M_n (corrected)	2406	3792	3163	2940	2705	2380	2028
M_w/M_n	2.56	2.17	2.23	3.44	1.56	3.67	4.38
Peak maximum	6318	8740	8740	9492	3262	9051	8862

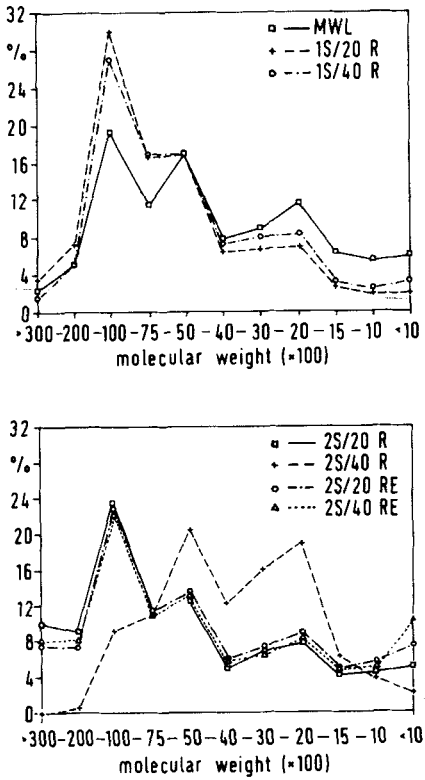

FIGURE 2: Frequency of molecular weight ranges according to Table 5

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Characterization of Molecular Weight Fractions

The demonstration plant lignin 2S/DA 1 was preparatively separated into 14 fractions of decreasing molecular weight (F 1 - 14). Surprisingly, F 2 despite having been eluted before F 3 on the Sephadex column, is characterized by lower M_w- and M_n-values than F 3 (Table 6). Obviously, the experimental conditions used for fractionation (high lignin concentration in 0.1 n NaOH) favour lignin association and preferentially affect the high molecular weight molecules[10]. In the subsequent HPSEC analysis, the lignins readily dissociate so that the particles are now eluted according to molecular size and not according to the size of associates. Elution profiles and M_w/M_n ratios indicate polydisperse fractions, with low molecular weight particles present in all fractions (Table 6, Figure 3). Nevertheless, despite these interactions M_w- and M_n-values of all fractions except F 2 are of a steadily decreasing order (from F 3 to F 10) and thus correspond to the elution volumes on the Sephadex column, so that the subsequently derived relationship between chemical structure and molecular weight is justified.

TABLE 6

MWD-Data of the Fractions from 2S/DA 1

Fraction	F 2	F 3	F 4	F 6	F 8	F 10
M_w	11240	11913	9076	5607	2851	2688
M_n	4709	6203	4407	2630	1602	1475
M_w/M_n	2.39	1.92	2.06	2.13	1.78	1.82

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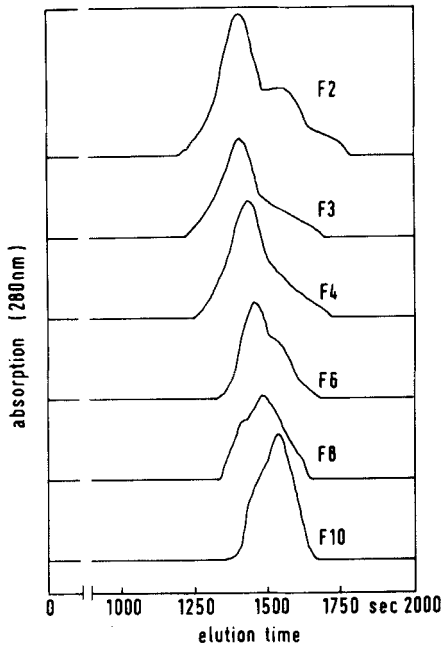

FIGURE 3: Elution profiles of the fractions of lignin 2S/DA 1

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Although functional group determination was confined to semi-quantitative estimations from ^{1}H-NMR-spectra, the results show unequivocally a preferential degradation of low molecular weight particles (F 8, F 10) during the cook. The ratio $OH_{Phen.}/OH_{Ali.}$ (F_{OH}) may be taken as an indicator for the degree of degradation. Starting with a F_{OH} of 0.35 for MWL (calculated from earlier data[2]) degradation reactions (increase of $OH_{Phen.}$ through ether cleavages, decrease of $OH_{Ali.}$ through side chain degradation) may shift F_{OH} to >1. Table 7 shows the correlation between F_{OH} and molecular weight: F_{OH} values continuously drop from 1.28 (F 10) to 0.51 (F 3 = highest molecular weight fraction).

Two alternatives appear feasible for explaining the underlying scheme for these reactions. The first one would be the protection of high molecular weight particles within lignin association complexes as evidenced by Garver and Sarkanen[15]. The formation of association complexes from Organocell lignins (M_w > 1 million) has recently been confirmed by laser light scattering experiments. Although acetylated samples were used, the bonding type assumed for these interactions (HOMO - LUMO) should be independent of the derivatization[20].

The other alternative involves the preference of distinct chemical structures which are typical for the lower molecular weight particles. Table 7 reveals a more pronounced side chain degradation of low molecular weight particles not only by means of high F_{OH}-values, but also by the decline of aliphatic protons ($H_{Ali.}$), while the aromatic signal range seems to be overlapped by vinylic structures, thus pretending abnormally high quantities of almost 3 $H_{Arom.}/C_9$ for F 10.
Thioacidolysis experiments indicate considerable enol ether formation during Organocell pulping, which is typical for sulfurfree alkaline processes[21]. Increasing amounts at enolethers in the low molecular weight fractions would certainly explain the changes concerning OH_{Ali} and H_{Ali} in Table 7. Enol ether formation, as well as condensation reactions at the C_5-atom, require phenolic units, which are more abundant in low molecular weight structures[21]. Thus, differences concerning the concentrations of the more reactive phenolic units may promote a preferential side chain degradation of low molecular weight lignins during Organocell pulping.

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TABLE 7

Analytical Data of the Fractions from 2S/DA 1

Fraction	C* (%)	H* (%)	O* (%)	MeO (C_9)	$OH_{Phen.}$ (C_9)	$OH_{Ali.}$ (C_9)	$OH_{Tot.}$ (C_9)	F_{OH}	$H_{Ali.}$ (C_9)	$H_{Arom.}$ (C_9)
F 2	63.99	5.94	30.07	0.93	0.51	0.80	1.31	0.64	4.17	2.30
F 3	63.64	5.73	30.63	0.93	0.46	0.90	1.36	0.51	3.78	2.28
F 4	62.42	5.64	31.94	0.91	0.51	0.81	1.32	0.63	3.30	2.56
F 6	64.29	5.80	29.91	1.13	0.55	0.77	1.32	0.71	3.09	2.53
F 8	63.74	5.84	30.42	1.11	0.68	0.79	1.47	0.86	3.02	2.77
F 10	65.32	5.92	28.76	1.00	0.72	0.56	1.28	1.28	3.19	2.91

* values are corrected for sugars and ash

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Differentiation between high and low molecular weight particles continues with the residual sugars (Table 8). Sugar concentrations drop from 2.91 % (F 3) to 0.27 % (F 10), while the individual sugar composition remains roughly the same. Thus, GPC fractionation yields slightly degraded high molecular weight lignins which are contaminated by residual sugars and almost sugarfree but highly degraded low molecular weight lignins.

TABLE 8

Sugar Composition of the Fractions from 2S/DA 1

Sugar		F 2	F 3	F 4	F 6	F 8	F 10
Rhamnose	%	-	-	tr	tr	tr	-
Mannose	%	0.78	1.01	0.75	0.55	0.27	0.06
Arabinose	%	tr	0.08	0.04	tr	0.03	tr
Galactose	%	0.97	0.95	0.66	0.45	0.22	0.12
Xylose	%	0.48	0.69	0.55	0.49	0.34	0.12
Glucose	%	0.67	0.51	0.36	0.21	0.13	0.04
ΣSugars	%	2.90	3.24	2.36	1.70	0.99	0.30
ΣPolysaccharides	%	2.60	2.91	2.12	1.53	0.89	0.27

tr = traces

CONCLUSIONS

HPSEC analysis of lignins according to the Organocell process revealed substantial differences between lignins of different origins (first stage, second stage, cooking residue) with regard to M_w and M_n. From the standpoint of a nonenergetic lignin utilization envisaged by Organocell GmbH the soluble lignins of the second stage are by far the most important samples. These lignins may be classified as low molecular weight lignins, with molecular weight ranges being similar to kraft lingins.

Little is known about the behaviour of lignin in solution. The investigation of a fractionated demonstration plant lignin is a first approach to this topic with regard to Organocell lignins. However, at the present stage of our research we are not yet able to evaluate the impact of association complexes on the overall structure of Organocell lignins. The complexity of this problem requires a continuing effort for elucidating the behaviour of Organocell lignins in solution, which may help to a better understanding of delignification reactions during Organocell pulping.

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