

New Aspects in Cationization of Lignocellulose Materials. III. Influence of Delignification on Reactivity and Extractability of TMAHP-Hemicelluloses

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Synopsis

Beech sawdust samples with different lignin content were alkylated with 3-chloro-2-hydroxypropyltrimethylammoniumchloride (CHMAC). The yields and the degree of substitution of trimethylammonium-2-hydroxypropyl (TMAHP) samples were similar. Differences were found in extractability of hemicelluloses from this materials both with water and dilute alkali. To obtain the maximum yield of TMAHP-hemicelluloses (ca. 90% of the amount originally present), it is sufficient to remove about 50% of lignin. The lignin component does not influence the reactivity of hemicelluloses. The isolated hemicelluloses differ only in the distribution of functional groups and extractability.

INTRODUCTION

The extent of alkylation of beech sawdust with 3-chloro-2-hydroxypropyltrimethylammoniumchloride (CHMAC) and the distribution of TMAHP substituents among the main wood components is connected with their reactivity and accessibility within the wood cell walls.^{1,2} It is evident that under optimal reaction conditions³ at most 50% of the original hemicelluloses could be removed in the form of TMAHP derivatives by water and dilute alkali extraction of unmodified wood sawdust.

This paper describes the effect of delignification pretreatment of beech sawdust on the extent of wood polysaccharide alkylation in order to elucidate the inhibition effect of lignin component on the reactivity and extractability of the hemicelluloses.

EXPERIMENTAL

Materials. Beech sawdust characterised previously¹ was delignified by sodium chlorite and acetic acid according to the method of Wise et al.⁴ The analytical data of native and delignified wood samples are in Table I. A 50 % aqueous solution of CHMAC was used as alkylating agent.

Methods. The activation with 3.5 and 17.5% water solution of NaOH for 30 min at 20°C and subsequent alkylation (material: NaOH:

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TABLE I
Composition of Native and Delignified Beech Sawdust (% of Dry Sample)

	Sawdust	Holocellulose I	Holocellulose II
Klason lignin	22.3	9.6	1.5
Cellulose	45.1	52.2	57.3
Hemicellulose	30.0	34.2	38.2

CHMAC = 1:0.3:0.7 weight relations) for 2 h at 60°C, as well as isolation of modified samples were described previously.^{2,3} The alkylated hemicelluloses were obtained from the modified samples by the fractional extraction with water and 5% NaOH. The isolation of the samples was done by dialysis and subsequent lyophilization.

The Klason lignin content, the exchange capacity, and the qualitative sugar analysis of the hydrolysates by GLC of trifluoroacetyl alditols were carried out as described previously.³ The cellulose and hemicellulose content of the samples was estimated from the D-glucose, resp. the sum of D-xylose, D-mannose, D-galactose, and D-arabinose, content of the hydrolysate after Klason lignin determination.

RESULTS AND DISCUSSION

In order to elucidate the influence of lignin on the alkylation of hemicelluloses and their extractability from wood, holocelluloses with different residual lignin content as well as native beech sawdust were used (Table I). The influence of activation on yield and exchange capacity of modified samples obtained by washing with 80% ethanol³ using constant reaction conditions can be seen from Table II. The presence of lignin did not prevent the alkylation of the polysaccharide component. The concentration of the used NaOH solution in the activation stage was the determining factor influencing the exchange capacity more strongly than the yield of modified samples. The higher degree of substitution was obtained after activation in 17.5% NaOH solution.

In Table III there are the results of fractional extraction of TMAHP-hemicelluloses obtained from modified beech sawdust as well as from two studied holocellulose samples. Under constant activation conditions (3.5 or 17.5% NaOH) the yield of water extractable TMAHP-hemicelluloses is increasing with increasing degree of delignification while the exchange

TABLE II
Characteristics of TMAHP-Modified Native and Delignified Beech Sawdust

Sample	Activation with			
	3.5 % NaOH		17.5 % NaOH	
	Yield (%)	Exchange capacity (mmol g ⁻¹)	Yield (%)	Exchange capacity (mmol g ⁻¹)
Sawdust	94.6	0.32	96.0	0.48
Holocellulose I	96.6	0.29	94.0	0.44
Holocellulose II	95.1	0.28	97.2	0.49

TABLE III
Yield and Exchange Capacity of Water and Alkali Extractable TMAHP-Hemicelluloses from the TMAHP Samples

Sample	Activation with NaOH (%)	TMAHP-hemicellulose fraction extracted with			
		Water		5% NaOH	
		Yield (%)	Exchange capacity (mmol g ⁻¹)	Yield (%)	Exchange capacity (mmol g ⁻¹)
Sawdust	3.5	8.1	1.14	12.2	0.29
	17.5	8.5	1.58	9.0	
Holocellulose I	3.5	12.7	0.80	15.0	0.49
	17.5	13.5	1.05	16.5	0.76
Holocellulose II	3.5	11.6	0.73	19.8	0.53
	17.5	19.2	1.20	15.4	0.84

capacity show a decreasing tendency. Both the yield and the exchange capacity of the alkali extractable TMAHP-hemicelluloses are higher after removal of lignin. This indicates that a more uniform distribution of the TMAHP substituents within the hemicellulose component takes place in the holocellulose samples. When about 60% of the lignin is removed (holocellulose I) the quantity of water extractable TMAHP-hemicellulose is increased, while their exchange capacity is slightly lower. This means that a greater quantity of hemicelluloses reacts with alkylating agent after a part of lignin has been removed. The molecular weight of the modified hemicelluloses also influences their solubility and extractability from TMAHP samples. A greater oxidative degradation of hemicelluloses by sodium chlorite is taking place with increasing degree of delignification.⁵ In this case the hemicellulose degradability with alkali is increased, and they become more soluble. The degradation of hemicelluloses during delignification and alkylation is influencing the yield ratio of water and alkali extractable TMAHP-hemicellulose (Table III). The proposed higher oxidative degradation of hemicelluloses by delignification in the case of holocellulose II resulted in a increase of alkali extractable fraction already at alkali concentration of 3.5% NaOH. The use of 17.5% of NaOH was accompanied by a greater extent of alkaline degradation during alkylation, and, consequently, the yield of water-soluble fraction of TMAHP-hemicellulose was increased. The most significant differences are in the yields of isolated TMAHP-hemicelluloses. These yields were increased from 60–70% to 81–88% (related to the original present amount) after about 60% of lignin (holocellulose I) had been removed. After removing the rest of lignin (holocellulose II) only a small increase (about 3%) was obtained.

The results of GLC analysis of the TMAHP-hemicellulose hydrolysates are in Table IV. The substituted TMAHP-saccharides were not included in the analysis. They represent about 5% of present saccharides. The molar ratio of D-glucose to D-xylose is practically constant (3–6/100). It means that the isolated fractions consist only of D-xylan.

By the previously mentioned isolation procedure of TMAHP samples from the reaction medium the whole polysaccharide portion was obtained. When

Sample	Extracted with	D-Xylose	D-Glucose	D-Mannose
Sawdust	Water	100	3.0	0
Holocellulose II	Water	100	4.0	0.5
Sawdust	5% NaOH	100	5.0	Traces
Holocellulose II	5% NaOH	100	6.0	1.5

TABLE IV
The Molar Ratios of Monosaccharides in the Hydrolysate of TMAHP-

TABLE V
 Characteristics of TMAHP Products after Eluation with Water and Extraction of the Solid Portion with 5% NaOH

Sample ^a	Solid portion		Water eluent		Extract	
	Yield (%)	Exchange capacity (mmol g ⁻¹)	Yield (%)	Exchange capacity (mmol g ⁻¹)	Yield (%)	Exchange capacity (mmol g ⁻¹)
Sawdust	83.1	0.14	14.4	3.2	1.3	0.36
Holocellulose I	69.5	0.28	19.0	1.2	11.9	0.38
Holocellulose II	65.0	0.32	27.4	1.0	7.4	0.78

^a All the samples were activated by 17.5% NaOH solution.

the TMAHP sample is eluted with water one part of TMAHP-hemicelluloses is extracted and another one remains in the solid fraction. The characteristics of samples prepared in this way are listed in Table V. In comparison to the results in Table III the hemicelluloses isolated as TMAHP derivatives from the water eluant of both holocellulose samples represent from 55 to 71% of the original present hemicelluloses and the exchange capacity is about 1.1 mmol g⁻¹. The whole quantity of extracted hemicelluloses remains the same as obtained by fractional extraction used for samples in Table III. From the practical point of view this procedure is more suitable for preparation of water-soluble TMAHP-hemicelluloses.

CONCLUSIONS

Lignin does not suppress the alkylation of wood polysaccharides with CHMAC but influences the distribution of functional groups and extractability of hemicellulose. Similar degrees of substitution and yields on modified sawdust samples with different lignin content were found. From the practical point of view it is sufficient to remove about 50–60 % of lignin to obtain the maximum yield of extractable hemicelluloses.

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