

New Aspects in Cationization of Lignocellulose Materials. II. Distribution of Functional Groups in Lignin, Hemicellulose, and Cellulose Components

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Synopsis

The distribution of functional groups in the three main components of beech after alkylation with 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) was studied. By fractional extraction of hemicellulose combined with delignification it was found that the three components were substituted to various extents. The exchanging capacity decreased in the following order: hemicellulose, lignin, and cellulose. The obtained degree of substitution is related to the accessibility and reactivity of the individual components in the wood. Hemicellulose, which is substituted the most, can be extracted from modified sawdust with water. This represents a new method of hemicellulose isolation from native plant materials.

INTRODUCTION

In our previous work¹ the most appropriate preparation conditions for derivatives of beech sawdust containing trimethylammonium-2-hydroxypropyl (TMAHP) groups with regard to the yield of solid and soluble portion were examined. From these results, however, no conclusions could be drawn about the distribution of the functional groups among the main components—cellulose, hemicellulose, and lignin. That is why the objective of this work is the complex analysis of modified sawdust by fractional extraction of hemicellulose combined with delignification.

EXPERIMENTAL

Materials. Beech sawdust characterized in our previous work was used as starting material. Three different samples of beech sawdust having different exchanging capacity, obtained under modification conditions given in our previous work, were used in the experiments. Sample A ($Q = 0.14$ mmol/g) was isolated from the reaction medium after neutralization with 1% HCl and water washing to negative reaction for chlorides. Sample B and C ($Q = 0.32$, resp. 0.48 mmol/g) were isolated from reaction mixture adding 96% ethanol and washing with 80% ethanol till washings were neutral (phenolphthalein).

Methods. The isolation of substituted cellulose, hemicellulose, and lignin from sample A was done by the scheme shown in Figure 1. Fractionation and delignification of sample B and C were done according to the scheme given in Figure 2. Holocellulose was determined according to Klaudivitz.² Hydrolysis of hemicellulose fractions was done with $2M$ F_3C $COOH$.³ The molar ratio of

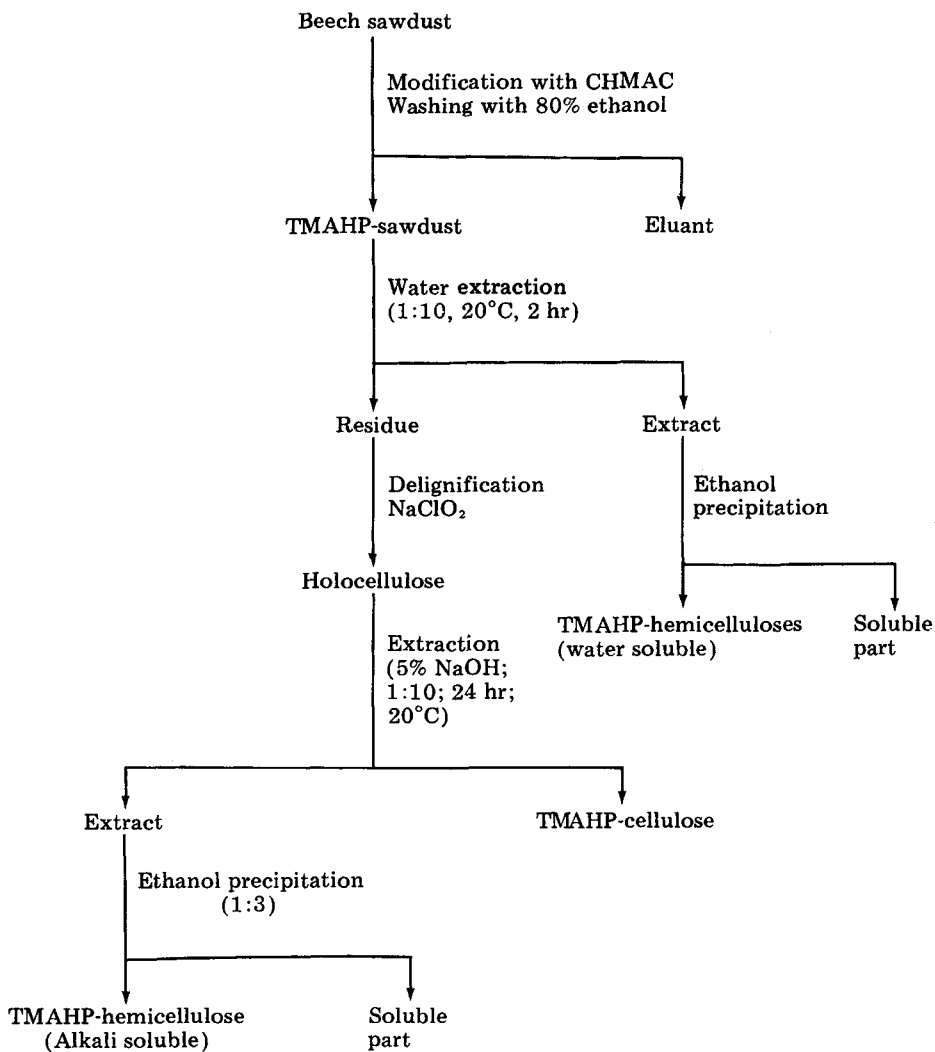


Fig. 1. Fractional extraction of TMAHP-sawdust (sample A).

neutral saccharides in the form of alditol trifluoroacetate was determined by GLC method.⁴ The isolation of dioxane lignin was made using a mixture of dioxane:water = 9:1 (vol) and 1% HCl at 100°C for 8 h. The rest of used methods was described in our previous work.¹

RESULTS AND DISCUSSION

To determine the degree of substitution with quaternary ammonium groups of the three main wood components modified sawdust was extracted according to the scheme given in Figure 1. A solid portion in the yield of 83.1% was obtained isolating TMAHP-sawdust from the reaction mixture by washing with water. A portion of higher substituted TMAHP-hemicellulose ($Q = 3.2$ mmol/g)

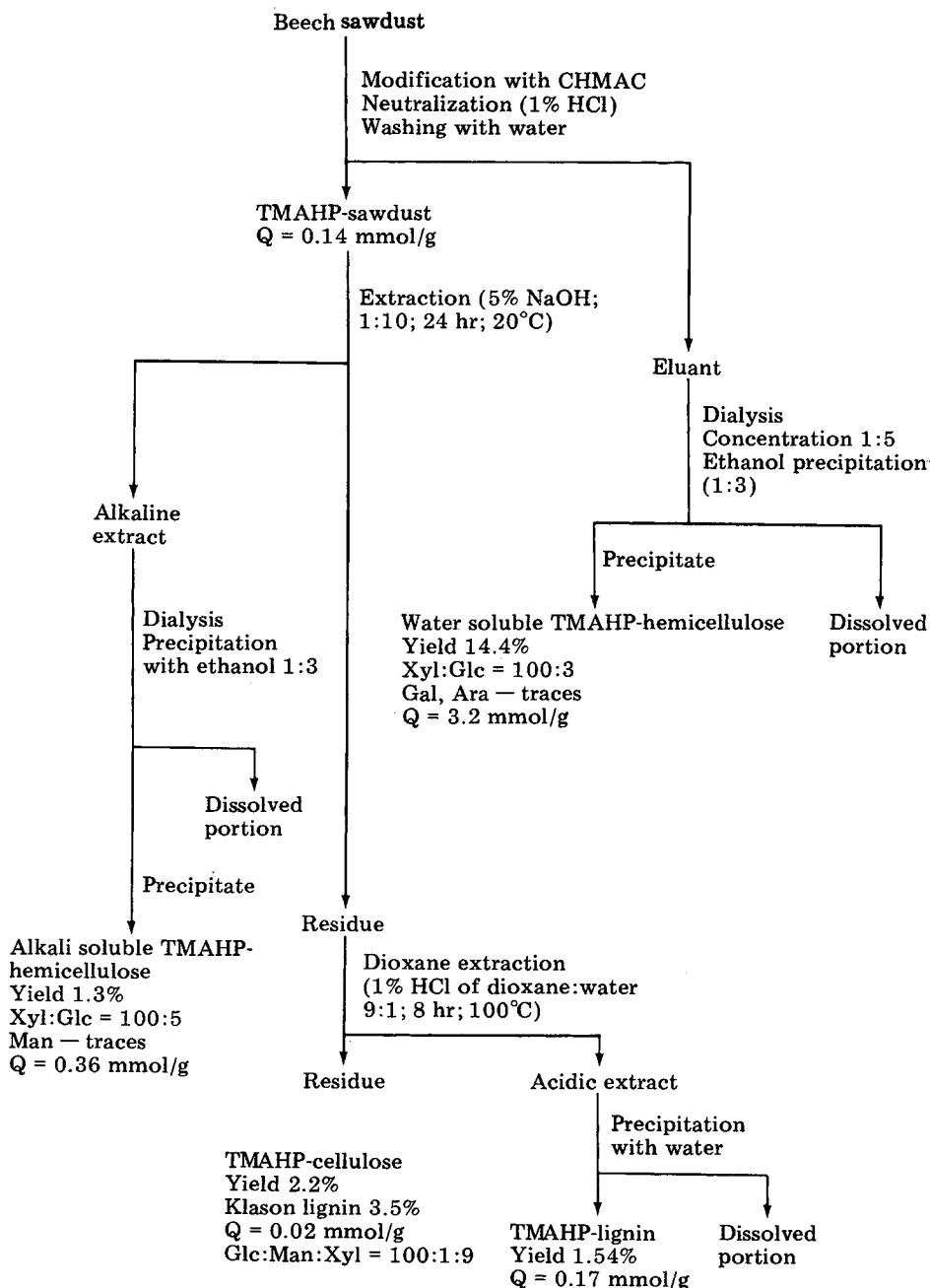


Fig. 2. Fractional extraction of TMAHP-sawdust (samples B and C).

in the amount of 14.4% was obtained from the eluents (all percentages are related to the original o.d. beech sawdust). The subsequent alkaline extraction of modified sawdust gave only 1.3% of hemicellulose with lower exchange capacity ($Q = 0.36$ mmol/g). From the chromatographic analysis of both hemicellulose

TABLE I
Sawdust Characteristics after Modification and Extraction of Sample A

Sample	Yield (%) ^a	Exchange capacity Q (mmol/g)	Klason lignin (%)	
			a	b
Beech sawdust	100	—	22.3	—
TMAHP-sawdust	83.1	0.14	20.7	24.9
Residue after alkaline extraction of hemicellulose	81.0	0.13	20.0	24.8
Residue after lignin extraction	42.2	0.02	1.5	3.5

^a Based on beech sawdust.

^b Based on TMAHP-sawdust.

fractions follows that they contained (4-*O*-methyl-D-glucurono)-D-xylane contaminated with small amounts of hexosanes. According to the content of Klason lignin in sawdust before and after modification and alkaline extractions (Table I), passed into the water eluent and the alkaline extracts together with hemicellulose only 1.6, resp. 0.7%, of lignin which remained dissolved after polysaccharide precipitation with ethanol. In this way a total amount of 50% originally present hemicellulose from the beech sawdust was obtained in the form of TMAHP-derivative without contamination with lignin. The majority of this portion was obtained by water extraction.

The dioxanalyses of the residue obtained after alkaline extraction of TMAHP-sawdust yielded gave the polysaccharide residue containing mainly cellulose with the lowest exchange capacity ($Q = 0.02$ mmol/g). From the acidic extract (yield 38.8%) into which passed 18.5% of lignin the dioxane TMAHP-lignin ($Q = 0.17$ mmol/g) in the yield of 1.5% was obtained by water precipitation. The decrease in the exchanging capacity of modified sawdust after dioxanalysis (Table I) in comparison with the exchange capacity of precipitated dioxane TMAHP-lignin (Fig. 1) showed that the soluble portion of the acidic extract was greatly substituted. The low yield of dioxane lignin is likely due to the increased solubility of its TMAHP-derivatives in the polar medium what was proved by alkylation of model lignin compounds with CHMAC.⁵ A part of highly substituted lignin could not be, therefore, precipitated from the acidic extract and remained in the soluble portion which contained also short polymer fractions of hemicelluloses and celluloses formed during dioxanalysis of lignocellulose materials. From the analyses it was impossible to determine the degree of substitution of the components in the soluble part of the acidic extract. This fractionation method made it possible to prove directly the distribution of functional groups only in the polysaccharide part. The degree of substitution of the whole lignin component was not determined by this method because it was impossible to isolate TMAHP-lignin in a representative amount.

To obtain further information about the substitution of the lignin component in modified sawdust we used the method of fractional extraction combined with delignification according to Figure 2. Fractional extraction was done with two samples of different exchange capacity, to be able to determine the effect of the substitution degree on functional groups distribution in the individual components of modified sawdust. The results of fractional extraction are given in Table 2. The modified sawdust were isolated from the reaction medium without

TABLE II
 Characteristics of Sawdust after Modification and Extraction of Samples B and C

	Sample B			Sample C				
	Yield (%)	Q (mmol/g)	Klason lignin (%)		Yield (%)	Q (mmol/g)	Klason lignin (%)	
			a	b			s	b
TMAHP-sawdust	94.6	0.32	22.1	23.4	96.0	0.48	21.6	22.5
Residue after water extraction	84.9	0.23	20.5	24.1	85.2	0.34	15.6	18.3
Hollocellulose	58.9	0.14	0.6	1.0	60.2	0.32	0.3	0.5
Cellulose	46.3	0.10	—	—	51.0	0.31	—	—
Water-soluble hemicellulose	8.1	1.14	—	—	8.5	1.58	—	—
Alkali-soluble hemicellulose	12.2	0.29	—	—	9.0	0.35	—	—

^a % Related to original beech sawdust.

^b % Related to modified beech sawdust.

neutralization only by ethanol elution. In this way the higher substituted TMAHP-hemicelluloses were retained in the product. This resulted in a higher yield and a substantially higher exchange capacity of TMAHP sawdust (Table II) in comparison to sample A. The mass balance showed that losses during isolation were approximately 5%, out of which 0.3–0.7% referred to the lignin component (Table III). The water extraction, similar to the first experiment, dissolved a part of higher substituted hemicellulose together with a part of lignin, which can be seen from the decrease of Klason lignin in an amount of 1.5–6% in modified sawdust after extraction. TMAHP-hemicellulose without lignin were isolated from the water extract by ethanol precipitation. The solid portion after water extraction was delignified by the NaClO_2 procedure with limited degradation of polysaccharides (Klauditz holocellulose). The decrease of exchanging capacity during delignification can be directly related to the degree of substitution in the removed lignin component. Out of the mass balance (Table II) followed for the lignin component of the samples A and B the exchange capacity 0.43 and 0.39 mmol/g. A similar exchange capacity was determined according to the content of nitrogen in Klason lignin for both samples of TMAHP sawdust. From the holocellulose prepared using samples 2 and 3 TMAHP-hemicelluloses were obtained by alkaline extraction having a lower exchange capacity (Table II) in comparison to water soluble TMAHP-hemicelluloses.

The obtained results showed that during the modification of beech sawdust with CHMAC all three components were substituted. The extraction residue represents TMAHP-cellulose having a exchange capacity 0.1 and 0.31 mmol/g. From Table III it can be seen that similarly as for sample A the hemicellulose fractions contained (4-*O*-methylglucurono)xylane and small amounts of hexosanes. The distribution of functional groups in the individual components depended on their accessibility and reactivity. In the biostructure of the wood cell hemicellulose and lignin are the most easily accessible components. The introduction of quaternary ammonium groups into macromolecules of the polysaccharides and lignin increases their hydrophilic character that results in increasing of their solubility in polar solvents. Thus up to 50% of hemicelluloses originally present in beech sawdust could be extracted with water in the form of TMAHP-(4-*O*-methyl-*D*-glucurone)xylane. By alkaline extraction further 25% of TMAHP-hemicellulose with lower substitution degree could be obtained. In the case of lignin a lower degree of substitution was found and in comparison to hemicellulose a lower portion could be extracted with water. The lower degree of substitution is connected with the structure of lignin which contained less free hydroxyl groups than the polysaccharide portion. Most of the reactive functional groups are blocked by lignin–lignin and lignin–saccharide bonds in the lignin–polysaccharide complex, and only a part can be liberated in alkaline medium and are able to react with CHMAC. The comparison of fractional extraction results of both samples (B and C) showed that in higher substituted TMAHP-sawdust the functional groups were distributed among the three components more uniformly. In this case, at the same degree of substitution of the lignin component, a greater amount of lignin was extracted with water, and a higher degree of substitution of the cellulose component was obtained. It is presumed that the previously mentioned fact is associated with the different activation method during the TMAHP-derivate preparation. It is evident that activation is a problem which must be examined in the future.

TABLE III
Analysis of Lignin and Hemicellulose Components of Modified Sawdust

TMAHP-sawdust	Klason lignin (%)		Exchange capacity Q (mmol/g)	Molar ratio of saccharides					
	a	b		Water-soluble hemicellulose		Alkali-soluble hemicellulose			
				Xyl	Glc	Man	Xyl	Glc	Man
Sample 2	23.3	22.0	(0.60) ^c 0.43	100	3.5	1	100	5	2
Sample 3	22.5	21.6	0.37 (0.52) ^c	100	4	0.5	100	6	1.5

^a % Related to original sawdust.

^b % Related to modified sawdust.

^c Calculated from nitrogen content.

CONCLUSIONS

By alkylation of beech sawdust with CHMAC all three components were substituted but to a different degree; the exchanging capacity decreased in the order: hemicellulose > lignin > cellulose. The obtained degree of substitution was dependent on the accessibility and reactivity of the individual components in wood. The component which was substituted to the highest degree—hemicellulose—could be extracted from modified sawdust with water. This may represent a new method for hemicellulose derivatives preparation directly from native plant materials.

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Received May 15, 1983

Accepted July 29, 1983