

New Aspects in Cationization of Lignocellulose Materials. IV. Modification of Aspen Wood Meal with Quarternary Ammonium Groups

MIROSLAV ANTAL, IVAN ŠIMKOVIC,* and ANNA EBRINGEROVÁ,
*Institute of Chemistry, Slovak Academy of Sciences, 842 38 Bratislava,
Czechoslovakia, and MICHAEL M. MICKO University of Alberta,
Department of Agricultural Engineering, Edmonton, Canada T6G 2G6*

Synopsis

Trimethylammonium-2-hydroxypropyl (TMAHP) derivatives of aspen wood were prepared by the reaction of wood meal with 3-chloro-2-hydroxypropyltrimethylammoniumchloride (CHMAC) in alkaline medium. The TMAHP sample was fractionated and yields and exchange capacities (Q) of individual fractions were compared with beech sawdust fractions obtained under the same conditions. The most evident difference between the two studied wood types was the higher yield (14.5% of starting material) of water-soluble TMAHP-hemicelluloses obtained from aspen wood.

INTRODUCTION

Lignocellulose waste materials are convenient as source of chemicals using microbial treatment or chemical hydrolysis. But these materials could also be used as the source of polymeric substances. In our previous papers the water-soluble TMAHP-hemicelluloses were extracted by water from beech sawdust, modified with CHMAC.^{1,2} The obtained yield of water-extracted TMAHP-hemicelluloses from this wood was as high as 8.5%.²

In the present study aspen wood meal was used as starting material. Aspen poplar trees are predominant in forests in Alberta but they are hardly used otherwise than as fire wood. With a view to more effective utilization of this material, we wanted to examine the properties of the TMAHP-aspen wood meal in comparison to the TMAHP-beech sawdust and to find out the differences between these two species. Preliminary examinations of TMAHP-derivatives from aspen wood meal were done in the foregoing study.³

EXPERIMENTAL

Materials. Wood meal (0.2–0.4 mm) from aspen wood (*Populus tremuloides* Michx.) was used as the lignocellulose material for alkylation. The content of aspen and beech main components and their solubilities in 1% NaOH is listed in Table I. The 50% (vol) aqueous solution of CHMAC was used as alkylating agent.

* Corresponding author.

TABLE I
Chemical Composition of Aspen and Beech Wood

Wood	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Solubility 1% NaOH (g dm ⁻³)
Aspen	57.2	25.6	17.2	187 ^a
Beech	45.1	32.6	22.3	175 ^b

^a From the literature.⁴

^b From the literature.⁵

Methods. The isolation of substituted cellulose, hemicelluloses and lignin was done according to the scheme shown in Figure 1. The rest of the methods used were described in our previous papers.¹⁻³

Preparation of the Sample. The aspen wood meal (70 g) was activated with 105 mL of 17.5% NaOH aqueous solution for 20 min at 20°C. The alkylating agent was added to the activated wood meal and the mixture was stirred for 4 h at 60°C. The reaction product was filtered and washed with 80% ethanol until neutral reaction was obtained (using phenolphthalein) and finally dried.

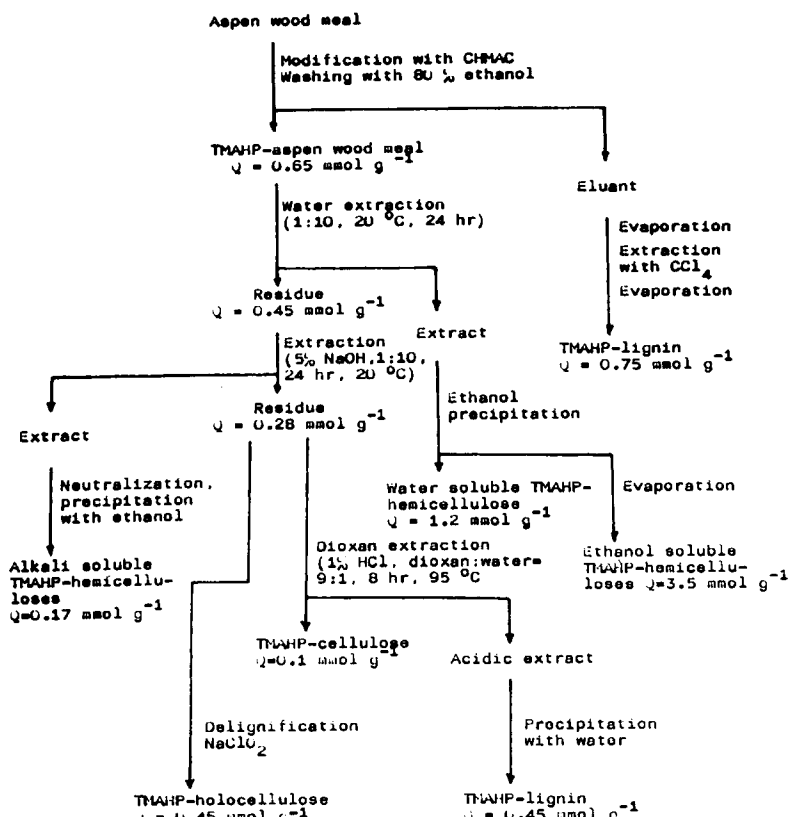


Fig. 1. Fractionation scheme of TMAHP-aspen wood meal.

RESULTS AND DISCUSSION

Aspen wood meal was modified with CHMAC and extracted according to the scheme shown in Figure 1. The solid portion after elution with 80% ethanol represents the TMAHP-aspen wood meal (95.7% yield, $Q = 0.65$ mmol g^{-1}). The value of ion exchange capacity was higher than that one obtained using beech sawdust (Table II) under similar conditions (0.48 mmol g^{-1}).² A part of lignin which had been degraded during activation and alkylation, dissolved in the eluant and was recovered by CCl_4 extraction. The hydrolyzed alkylating agent was separated from TMAHP-lignin fraction ($Q = 0.75$ mmol g^{-1}). The composition of this fraction was proved by¹³C-NMR. There were no signals related to carbohydrates in the spectrum. The signals in the spectrum were 55 ppm (methyl group of TMAHP substituent), 57 ppm (OCH_3 group), 63 ppm (C- γ in β -0-4), 66, 67, and 68.5 ppm (C- γ in phenylcoumarans) and 153 ppm (oxygen-substituted aromatic ring carbon).⁴

The TMAHP-wood meal was further extracted with water and the extract precipitated with ethanol. The water-soluble TMAHP-hemicelluloses obtained in this way (14.5% of starting material) contained 1.2 mmol g^{-1} of quarternary ammonium groups. The presence of TMAHP group in hemicellulose molecule was proved by ¹³C-NMR in the previous work.³ The ion exchange capacity of this sample is lower than the one determined for beech sawdust TMAHP-hemicellulose. The water soluble part which could not have been precipitated by ethanol represents 2.7% of the starting material and had the highest exchange capacity (3.5 mmol g^{-1}). The residue after water extraction represented the rest of the hemicelluloses, the part of lignin, and the whole cellulose component. The exchange capacity of this portion was still quite high (0.45 mmol g^{-1}). The small fraction of alkali-soluble TMAHP-hemicelluloses (1.3% yield) with lowest exchange capacity ($Q = 0.17$ mmol g^{-1}) was obtained by 5% NaOH extraction of the water-insoluble residue. The insoluble portion containing 0.28 mmol g^{-1} of quarternary ammonium groups was extracted with dioxan and separated in two (lignin-rich and cellulose-rich) fractions with ion exchange capacities of 0.45 mmol g^{-1} and 0.1 mmol g^{-1} , respectively.

TABLE II
Comparison of the Yields and Exchange Capacities of Beech and Aspen Samples Obtained by the Fractionation

Sample	Beech		Aspen	
	Q (mmol g^{-1})	Yield (%)	Q (mmol g^{-1})	Yield (%)
TMAHP-wood	0.48	96.0	0.65	95.7
TMAHP-residue after water extraction	0.34	85.2	0.45	78.5
TMAHP-holocellulose	0.32	60.2	0.45	65.7
Water-soluble TMAHP- hemicellulose	1.58	8.5	1.2	14.5
Alkali-soluble TMAHP- hemicelluloses	0.35	9.0	0.17	1.3

Some evident differences were found (Table II) in hemicelluloses yields by comparison of the results obtained from the beech and aspen wood. The yield of alkali-soluble beech wood TMAHP-hemicelluloses is higher than for aspen TMAHP-hemicelluloses due to the difference in fractionation procedure. In our previous work we found that TMAHP-hemicelluloses isolated from the alkylated holocellulose sample are more degraded than those isolated without previous delignification.⁵ That is why we did not use the holocellulose procedure in the fractionation of the modified aspen wood before alkali extraction. The holocellulose isolated from the TMAHP-aspen wood after water and alkali extractions is higher in both, yield (65.7%) and exchange capacity (0.45 mmol g^{-1}), as compared to the holocellulose from the corresponding TMAHP-beech sawdust (60.2% yield, $Q = 0.32 \text{ mmol g}^{-1}$). The reason for this result might be due to higher cellulose content of aspen wood. It seems that the cellulose component of aspen wood was less accessible for alkylation ($Q = 0.1 \text{ mmol g}^{-1}$) than the beech sawdust cellulose portion ($Q = 0.31 \text{ mmol g}^{-1}$).

Although the yields of aspen and beech TMAHP-wood samples were practically identical, the aspen wood showed up with the higher degree of substitution (Table II). This results might be related to the accessibility of hemicellulose fraction. While the quantity of hemicelluloses present in aspen is about 7% lower than in beech wood, the yield of water-soluble TMAHP-hemicelluloses obtained under the same conditions is 6% higher. This corresponds to the known higher accessibility of the morphological structure and the extractability of native aspen wood in 1% NaOH (Table I) as compared with beech wood.^{6,7} The results obtained indicate differences in the distribution of hemicelluloses within the cell wall layers of both studied wood samples. Most of the aspen hemicelluloses are probably located in outer layers of the cell wall and therefore were more easily accessible to the attack of chemicals. An additional difference is the lower lignin content (about 5%) of aspen wood. This may also contribute to the extractability of the aspen hemicelluloses.^{6,7}

From the practical point of view, aspen wood is more suitable for preparation of TMAHP-hemicelluloses than beech wood even though the hemicellulose content of aspen is lower.

CONCLUSIONS

TMAHP derivatives with the exchange capacity of 0.65 mmol g^{-1} and the yield of 95.7% from aspen wood meal were prepared. All three components of wood were substituted. Their exchange capacity decreased in the following sequence: TMAHP-hemicelluloses > TMAHP-lignin > TMAHP-cellulose. The degree of substitution of the aspen hemicelluloses fraction was not higher than that of beech sawdust. TMAHP-hemicelluloses with 1.2 mmol g^{-1} of quarternary ammonium groups could be extracted from TMAHP-aspen wood meal with water in 14.5% yield which is 56.6% of the original hemicelluloses. This represents a very convenient method for isolation of cationic hemicelluloses from aspen wood meal.

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