New Aspects in Cationization of Lignocellulose Materials. I. Preparation of Lignocellulose Materials Containing Quarternary Ammonium Groups

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Synopsis

TMAHP derivatives were prepared by the reaction of beech sawdust with CHMAC in alkaline medium. The examination of the reaction conditions showed that the most suitable molar ratio was NaOH/CHMAC = 1.8 (1 mL 17.5% NaOH/1 mL 50% CHMAC). At this ratio the maximum degree of substitution expressed by the exchange capacity of 0.35 mmol/g of modified sawdust was obtained by using 1.5–2 mL of 50% aqueous solution of CHMAC/g sawdust. The optimal reaction time at 60°C was 2 h. This condition gave yields of modified sawdust above 90% and soluble derivatives mainly consisting of hemicelluloses up to 12%.

INTRODUCTION

Derivatives based on lignocellulose materials are finding growing application in chemistry and technology of wood and paper. The chemical modification of these materials with quartenary ammonium group can improve or change many properties. So far by this method the improvement of pulp properties from the paper-technical point of view,[1] with increase of cotton affinity to reactive dyes,[2,3] and the protection against biodegradation[4] were investigated in cellulose processing. For the time being, the main interest was given to cellulose derivatives which prove to be useful as additives in production of paper[5] and in the production of electric conductive layers.[6] Lignin[7] and hemicelluloses[8–10] from different raw materials were studied only rarely. An important fact is that many lignocellulose materials are industrial waste, which is most often burned because this seems to be the most economic way of their use at the present time. The objective of our work is to improve the application of carbohydrate polymers in industry by mean of cationization of lignocellulose material. With regard to the fact that preparation of isolated polysaccharides (cellulose, hemicelluloses) is is expensive (energy, chemicals), the derivative of polysaccharides obtained by modification of native materials could be progressive. This would contribute to the more complex use of wood material.

This work studies the preparation of trimethylammonium-2-hydroxypropyl (TMAHP) derivative of beech sawdust. As alkylation agent 3-chlor-2-hydroxypropyltrimethylammoniumchloride (CHMAC) was used. This agent contains the α-halohydrine function group which can form in alkaline media etheric bonds with hydroxyl groups of polysaccharides or with the aliphatic and aromatic hydroxyl groups of the lignin component of wood. For maximal reduction of undesirable hydrolysis of the alkylation agent CHMAC in alkaline

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media it is required to determine the most suitable reaction parameters. It is necessary to know the effect of the individual components of the reaction mixture upon the course of reaction. That is why the time and concentration dependence, the effect of activation, and the ratio of reaction components on the degree of substitution and yield of modified product were examined.

EXPERIMENTAL

Materials. Sawdust (0.2–4 mm) prepared from bark-free beech trunk (Fagus silvatica) extracted with the mixture of benzene/alcohol was used as lignocellulose material. The contents of the main component were: lignin 22.3%, cellulose 45.1%, and hemicellulose 32.6%. The 50% vol. aqueous solution of CHMAC was used as alkylating agent.

Methods. The quantitative content of quarternary ammonium groups was determined using potentiometric titration as follows: the amount of 50 mL 1*M* aqueous solution of NaCl was added to 1 g of TMAHP–beech sawdust in the OH^- form and was let stand for 12 h. Titration with 0.1*M* aqueous solution of HCl was done during continuous mixing. The change of pH was recorded using the combined electrode. The exchange capacity was calculated according to the equation

$$Q = \frac{sf}{10m} \quad \text{(mmol/g)}$$

where s = amount of 0.1*M* HCl (mL) corresponding to the equivalent point, f = factor of the used 0.1*M* HCl, m = weight of absolute dry TMAHP–beech sawdust (g). The yield of modified product was expressed as percentage related to the original material, by the equation

$$\text{yield} = \frac{n(1 - 0.134Q) \times 10^4}{n_0 p}$$

where n = weight of absolute dry TMAHP–beech sawdust, Q = exchange capacity (mmol/g), n_0 = weight of air-dried sawdust, p = dry substance (%). The value of 0.134 corresponded to 1 mmol of functional group in the OH^- form. Klason lignin was determined according to Tappi Standard T 13 m-54.

Preparation of Samples. The beech sawdust was activated with 1.5 mL of 17.5% aqueous solution of NaOH for 1 g of sawdust during intensive mixing at 20°C for 20 min. The alkylating agent was added to the activated sawdust and mixed continuously at 60°C. The reaction product was washed with distilled water until neutral reaction was obtained (using phenolphtalein). After water elimination with aceton, the sample was vacuum-dried at 40°C to constant weight. The qualitative composition of the individual components in the reaction mixture is found in the descriptions of the figures.

RESULTS AND DISCUSSION

It is necessary to activate the lignocellulose material before alkylation (ionization of functional groups, increase of accessibility) which is mostly done with aqueous solution of NaOH. In our experiments 17.5% NaOH in the amount 1.5 mL/g (7.8 mmol/g) of sawdust were used which was the optimal condition also

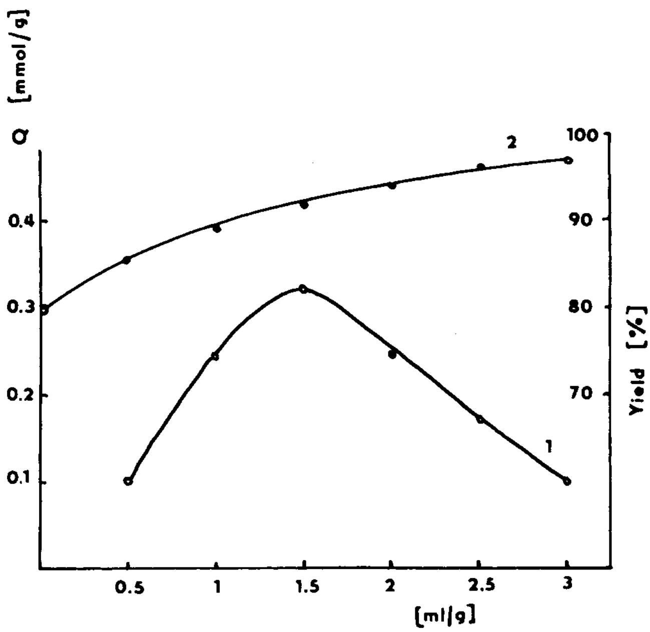

Fig. 1. Dependence of exchanging capacity Q (curve 1) and yield of modified sawdust (curve 2) on the amount of added CHMAC during activation with 1.5 mL 17.5% NaOH/g of sawdust.

for the reaction of cellulose with diethyl-2,3-epoxypropylamine.[11] At lower hydroxide concentration, the side reaction—hydrolysis of the alkylating agent—is noted; at higher concentration the reaction of opening and epoxide ring which is formed as intermediate from α-halohydrine[12] is suppressed.

Figure 1 shows the studied effect of the added amount of CHMAC on the substitution degree of the obtained product, expressed by the exchange capacity. The maximum value of exchange capacity, obtained at 1.5 mL 50% aqueous solution of CHMAC or 4.2 mmol/g of sawdust, which corresponds to the molar ratio NaOH/CHMAC = 1.8 can be seen in Figure 1 (curve 1). At lower amounts of alkylating agent a lower exchanging capacity is obtained, resulting from side reaction; with a surplus of alkylating agent its value decreases as the result of insufficiency of hydroxide in the reaction medium. In dependence on the content of NaOH in the reaction mixture (Fig. 1—curve 2) in the case of surplus of alkali losses of the material occur resulting from the extraction of some components of the lignocellulose material. In the case of greater amount of alkylating agent as 1.5 mL/g sawdust the yield of modified material increases moderately, simultaneously with decrease of the exchanging capacity, because the extraction of the components is suppressed by the insufficiency of alkali.

At the constant ratio of NaOH/CHMAC (1.5 mL 17.5% NaOH/1.5 mL 50% CHMAC), which was found during the optimation of the reaction parameters, the time dependence at 60°C was studied (Fig. 2). After 2 h of alkylation the exchanging capacity remained unchanged and that is why we worked in all experiments with the reaction time of two hours.

Figure 3 shows the effect of diluting the mixture of sawdust and 17.5% NaOH with water in the alkalization step on yield and exchanging capacity of the modified product. The decrease of NaOH concentration causes an intensive

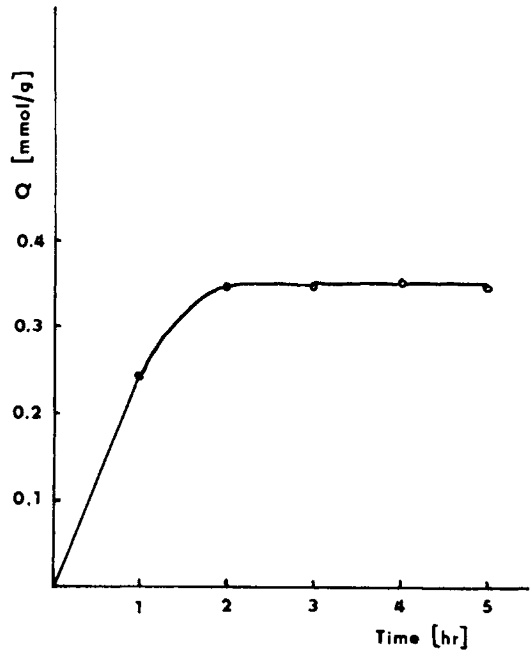

Fig. 2. Alkylating time effect on exchanging capacity of modified sawdust during alkylation with 1.5 mL 17.5% NaOH/1.5 mL 50% CHMAC on 1 go of sawdust at 60°C.

decrease of the exchanging capacity (curve 1) at practically unchanged yield (curve 2). These results confirm the optimal 17.5% concentration of NaOH solution, because the dilution favors the hydrolysis of CHMAC.

The dependence of the exchanging capacity on the amount of added CHMAC at optimal ratio NaOH/CHMAC (1 mL 17.5% NaOH/1 mL 50% CHMAC) is shown in Figure 4 (curve 1). It was found that it is no-advantage to increase the amount of alkylating agent above 1.5–2 mL/g sawdust, because the exchanging capacity increases only slightly. On the other side, the decrease of modified sawdust yield is found when the amount of alkylating at constant ratio of NaOH/CHMAC was increased in the reaction mixture (Fig. 4, curve 2); this can be explained by the increased substitution of extracted components.

By the modification of beech sawdust with CHMAC in alkaline medium two portions are obtained—solid part (modified sawdust) and soluble part. The study of the reaction conditions showed that it is possible to obtain the maximum degree of substitution expressed by the exchanging capacity 0.35 mmol/g for TMAHP–sawdust. For comparison of the degree of substitution, it is necessary to consider not only the amount of used alkylation agent but also the yield of the solid portion. Out of the experiments it follows that this is obtained at 1.5–2 mL CHMAC/g sawdust. This condition gives 91–92% yield of solid part with regard to the original sawdust. At increased amount of alkylation agent the substitution degree remained practically unchanged, but at decreasing yield of solid portion.

With regard to the fact that the modification of beech sawdust is done in the presence of dilute alkaline solutions the extraction of certain components of lignin and hemicelluloses,[13] which are in the surface cell wall layers of wood, can be expected. These components are not only more readily accessible, but also more

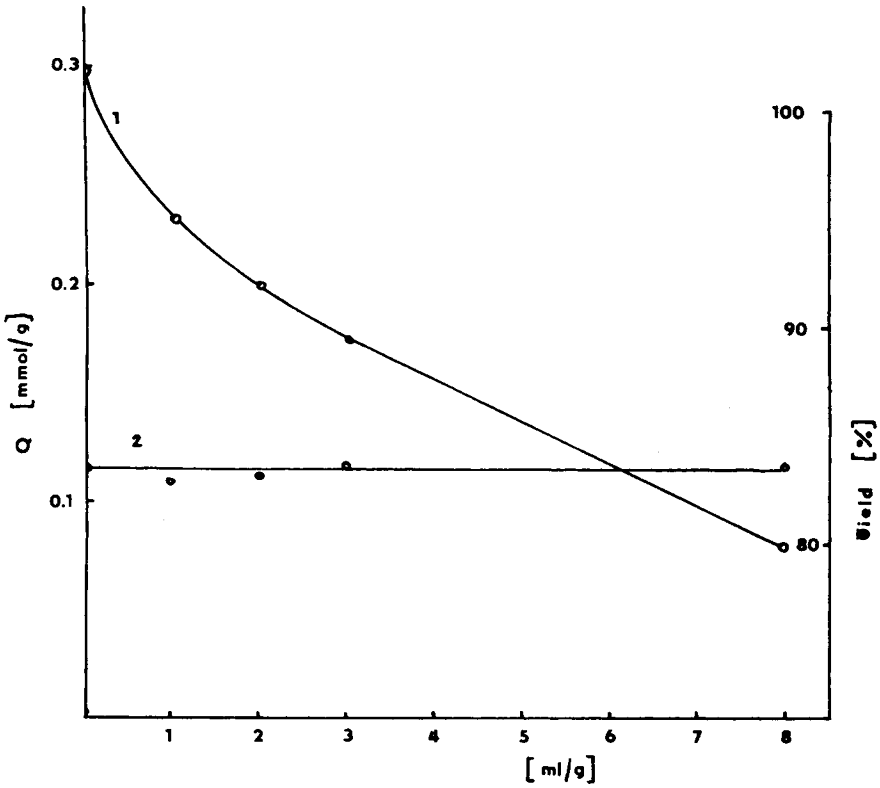

Fig. 3. Effect of dilution with water on the exchanging capacity (1) and yield of modified sawdust (2) in alkylation with 1.5 mL 17.5% NaOH/1.5 mL 50% CHMAC on 1 g of sawdust.

reactive in comparison to cellulose. They obviously form the dissolved portion obtained during modification the solubility of which is affected by the substitution degree. To evaluate the whole course of beech sawdust modification, it is necessary to consider also the substitution degree of the dissolved portion. That is why in further experiments the solubility of this part was controlled. In the isolation of modified sawdust from the reaction mixture 96% ethylalcohol instead of water was used to finish the reaction and for the washing 80% ethylalcohol was applied. In this way the low molecular inorganic and organic products were also removed. The exchanging capacity of the product isolated by this method and its yield are shown in Figure 4 (curves 1a, 2a). They confirm the presence of highly substituted soluble components in the amount of 10–12%. The yield and degree of substitution increase with increasing amount of alkylating agent. This is evident mainly at the ratios above 2 mL CHMAC/g sawdust. With regard to the fact that the decrease of modified sawdust weight (Fig. 4—curve 2) was greater than the changes of Klason lignin (curve 3) we draw the conclusion that the soluble portion contained mainly hemicelluloses.

Beech sawdust as native material is characterized by the undisturbed biostructure. This is why the effect of alkali and alkylating agent is limited only to the surface of cell walls. This determines the topochemical character of the reaction. The network structure of lignin covers the cell surface and inhibites the swelling of the cellulose and in this way also its activation. We propose that by a suitable way of delignification it could be possible to improve the accessibility

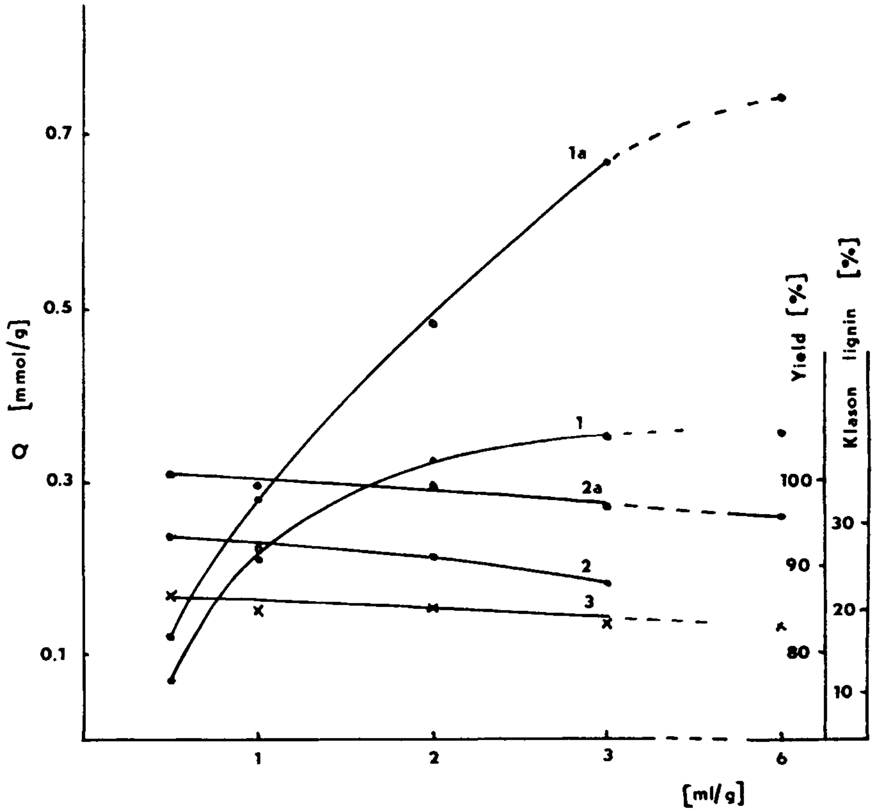

Fig. 4. Dependence of exchanging capacity, yield, and content of Klason lignin of the solid portion on the amount of added CHMAC at constant volume ratio 17.5% NaOH/50% CHMAC = 1:1. The results represent: (1) exchange capacity; (2) yield; (3) Klason lignin of the solid portion; or (1a) exchanging capacity; (2a) yield of solid portion isolated using ethanol.

of the whole polysaccharide component and to obtain a higher substitution degree of the solid part and an increased yield of the soluble derivatives of hemicellulose.

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