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Preparation of microcrystalline cellulose aminoderivatives

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Cellulose aminoderivatives were prepared by the reaction of microcrystalline cellulose (MCC) with alkylating agents 3-chlor-2-hydroxypropyltrimethylammonium chloride (CHMAC) and 1,3-bis(3-chlor-2-hydroxylpropyl) imidazolium hydrogensulphate (BCHPIHS) in an alkaline medium. The examination of the reaction parameters showed the most suitable molar ratio of NaOH/CHMAC to be 1·2 (1·5 ml 17·5% NaOH/2·5 ml CHMAC per 1·00 g MCC). At this ratio, the maximum degree of MCC substitution, expressed by the exchanging capacity of trimethylammonium hydroxypropyl (TMAHP) for MCC, was obtained (0·94 mmol/g). By reaction of MCC with BCHPIHS, the optimal molar ratio NaOH/BCHPIHS was 3·00 (4·5 ml 17·5% NaOH/2·4 ml BCHPIHS per 1·00 g MCC). At this molar ratio, the maximum exchanging capacity of 1·56 mmol/g of bis(hydroxypropyl) imidazolium (BHPI) MCC was obtained. The optimal reaction time at 60° C was 2–3 hours.

INTRODUCTION

In our previous papers, the preparation of various types of lignocellulosic materials containing quaternary-ammonium groups was reported. They were mainly TMAHP and BHPI derivatives. The optimal reaction parameters were found for the preparation of TMAHP and BHPI derivatives of the lignocellulosic materials (Antal *et al.*, 1984*a*; Šimkovic *et al.*, 1987). By fractional extraction of hemicelluloses combined with delignification, it was found that all three components (cellulose, hemicelluloses, and lignin) were substituted to various degrees. The degree of substitution obtained was dependent on the accessibility and reactivity of individual components in the wood matrix and decreased in the order hemicelluloses > lignin > cellulose (Antal *et al.*, 1984*b*).

It is important to know the behaviour of all three main components of the lignocellulosic materials during modification with CHMAC and BCHPIHS. In this paper, the optimum reaction parameters for the preparation of TMAHP and BHPI derivatives of microcrystalline cellulose are examined.

EXPERIMENTAL

Materials

Microcrystalline cellulose Bukoza, Vranov, Czechoslovakia (mesh 70–400) was used. Aqueous CHMAC (50% (vol.)) and aqueous BCHPIHS (93% (vol.)) were used as alkylating agents (Spolek pro Chemicku a Hutni Vyrobu, Usti nad Labem Czechoslovakia).

Methods

The quantitative content of quaternary-ammonium groups was determined by using potentiometric titration as described in our previous paper (Antal *et al.*, 1984*a*).

Preparation of samples

TMAHP MCC

Microcrystalline cellulose (MCC) (1·00 g) was activated with a 17·5% aqueous solution of NaOH (0·75–4·5 ml) during intensive mixing at 20°C for 20 min. CHMAC

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(2·5 ml) was added to the activated MCC and mixed continuously at 60°C. The reaction product was washed with distilled water until a neutral reaction was obtained (by using phenolphthalein indicator). After the elimination of water with acetone, the sample was vacuum-dried at 40°C to constant weight.

BHPI MCC

Microcrystalline cellulose (1·00 g) was activated with a 17·5% aqueous solution of NaOH (1·5–6 ml) during intensive mixing at 20°C for 20 min. BCHPIHS (2·4 ml) was added to the activated MCC and mixed continuously at 60°C. For isolation of the products, the same procedure as for TMAHP MCC was used.

The quantitative composition of the individual components in the reaction mixture, the reaction time, and the temperature are given in Tables 1–3.

RESULTS AND DISCUSSION

It is necessary to activate MCC before alkylation (ionization of functional OH groups and increased accessibility). This is mostly done with aqueous NaOH solution. In our experiments, 17·5% NaOH was used. This is also the optimal concentration for the reaction of cellulose with diethyl-2,3-epoxypropylamine (Antal, 1980). At a lower sodium hydroxide concentration, the reaction of the opening epoxide ring, which is formed as an intermediate product from alpha-halohydrine, is suppressed (Kaufer *et al.*, 1980).

It is evident from Table 1 that the most suitable molar ratio of NaOH/CHMAC for the preparation of TMAHP MCC is 1·20. This value is lower than that in the case of TMAHP beech sawdust, for which the optimal molar ratio was 1·80 (Antal *et al.*, 1984*a*). The higher molar ratio of NaOH/CHMAC for the preparation of TMAHP beech sawdust was due to the carboxyl and acetyl groups present in sawdust. The carboxyl and acetyl groups consume the sodium hydroxide to exchange H with Na ions, and consequently the optimal molar ratio of NaOH/CHMAC was higher. At lower amounts of CHMAC, a lower exchanging capacity is obtained owing to a side reaction (hydrolysis of alpha-halohydrine groups of CHMAC). In the case of a surplus of CHMAC, the value of the exchanging capacity decreases as a result of the insufficiency of sodium hydroxide in the reaction medium.

For the preparation of BHPI MCC derivatives, as is shown in Table 2, the optimal molar ratio of NaOH/BCHPIHS is 3·00. It is more than twice as high as TMAHP MCC derivatives. This is mainly due to the different chemical structures of BCHPIHS and CHMAC. BCHPIHS is a bifunctional reagent containing two halohydrine groups on the imidazole molecule. Most probably, during the reaction between MCC and BCHPIHS in an alkaline medium, a cross-linking reaction takes place. The two alpha-halohydrine groups of the BCHPIHS consume twice as much sodium hydroxide as the one alpha-halohydrine of the CHMAC. This results in a higher optimal molar

Table 1. Dependence of exchanging capacity (EC) of TMAHP MCC on molar ratio (MR) of reaction components

MCC (g)	CHMAC (ml)	NaOH (ml)	MR: NaOH/CHMAC	EC (mmol/g)
1·00	2·50	0·75	0·60	0·30
1·00	2·50	1·50	1·20	0·94
1·00	2·50	3·00	2·40	0·52
1·00	2·50	4·50	3·60	0·41

Reaction time 2 hours.
Reaction temperature 60°C.

Table 2. Dependence of exchanging capacity (EC) of BHPI MCC on molar ratio (MR) of reaction components

MCC (g)	BCHPIHS (ml)	NaOH (ml)	MR: NaOH/BCHPIHS	EC (mmol/g)
1·00	2·40	1·50	1·00	0·16
1·00	2·40	3·00	2·00	1·16
1·00	2·40	4·50	3·00	1·52
1·00	2·40	6·00	4·00	0·44

Reaction time 2 hours.
Reaction temperature 60°C.

Table 3. Dependence of exchanging capacity of BHPI MCC on reaction time

Reaction time (min)	Exchanging capacity (mmol/g)	Reaction time (min)	Exchanging capacity (mmol/g)
15	0·18	60	0·82
30	0·40	120	0·92
45	0·62	300	0·94

Molar ratio NaOH/BCHPIHS 3·00 (2·25 ml NaOH and 1·2 ml BCHPIHS).
Reaction temperature 60°C.

ratio of NaOH/BCHPIHS in the preparation of BHPI MCC derivatives.

The time-dependence at 60°C was also studied at the constant molar ratio of NaOH/BCHPIHS of 3·00. This ratio was determined during the optimization study for the reaction parameters. Table 3 summarizes the exchanging capacity for BHPI MCC derivatives as a function of the reaction time. The increase in exchanging capacity is directly proportional during the initial stages of reaction (the first hour) and then levels off between one and two hours. After two hours of MCC modification with BCHPIHS, the exchanging capacity remained practically unchanged. Consequently, all experiments were done at a reaction time of two hours (Tables 1 and 2). At a lower reaction temperature (20°C), the exchanging capacity increases proportionally over a longer reaction time until it levels off after 20–24 hours at a maximum degree of substitution as listed in Table 3. Comparing the results given in Tables 2 and 3, one can observe the following differences in reported exchanging capacities. Under the optimal reaction conditions for two parameters, a molar ratio of NaOH/BCHPIHS of 3·00 and a reaction time of 2·00 hours, the exchanging capacities are 1·52 mmol/g and 0·92 mmol/g, respectively. This difference is caused by the various amounts of NaOH and BCHPIHS added to 1·00 g of MCC. In the experiments of Table 2, there are 4·5 ml of 17·5% NaOH and 2·4 ml of BCHPIHS as compared with the addition noted in Table 3 of 2·5 ml of 17·5% NaOH and 1·2 ml of BCHPIHS.

CONCLUSIONS

The MCC was modified with CHMAC and BCHPIHS in an alkaline medium, which resulted in a product of TMAHP and BHPI derivatives. The optimal molar ratio of NaOH/CHMAC was 1·2. Under these conditions, the TMAHP derivatives of MCC have an exchanging capacity of 0·94 mmol/g. The optimal molar ratio for the preparation of TMAHP MCC derivatives is lower than that for the similar TMAHP derivative prepared from beech sawdust. The optimal NaOH/BCHPIHS molar ratio for the preparation of BHPI MCC was 3·00. Under these conditions, BHPI MCC derivatives with an exchanging capacity of 1·56 mmol/g were obtained. The optimal reaction time at 60°C for the preparation of both TMAHP and BHPI derivatives was two hours. The higher molar-ratio value for the NaOH/BCHPIHS system is due to the alkylating agent containing two alpha-halohydrine groups.

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