

STUDIES ON CARBOXYMETHYLCELLULOSE

Part III.—Direct Carboxymethylation of (Impure) Jute

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Jute powder was directly carboxymethylated with sodium hydroxide and chloroacetic acid in the ethanolic medium. It appears that delignification by chloroacetic acid itself and ethanol precedes the main reaction; and the jute cellulose being available in a reactive state, it could be carboxymethylated to a higher degree (upto a maximum of 1.48). Optimum conditions have been worked out and a flow-sheet given. A by-product has been obtained which can be used as an adhesive.

Introduction

In Part I of this series¹ it was reported that sodium carboxymethylcellulose having a relatively high D.S. and possessing emulsifying properties could be prepared from carefully purified jute cellulose; but the operation entailed the use of 50-70 per cent sodium hydroxide, which among other difficulties could cause degradation of the cellulose chain. This difficulty was overcome in a subsequent work² by the use of aqueous organic solvents. A number of aliphatic alcohols (and benzene) were studied and best results were obtained with ethyl alcohol. With this, under optimum conditions, a degree of substitution of upto about 1.30 (in single treatment) was obtained, using an alkali concentration of only 17%. Hot ethanol is known to extract lignin from cellulosic material in slightly acidified medium; monochloroacetic acid also has been reported³ to react with lignin. On the basis of this, it was interesting to study the effect of using the jute fibre without prior delignification in the carboxymethylation. In the present investigation it has been demonstrated that the simultaneous delignification and carboxymethylation can be effectively carried out with alkali and chloroacetic acid in an aqueous ethanolic medium. Optimum conditions have been established for obtaining a product having a D.S. of 1.48. Further, a by-product can also be obtained during purification which can be used as an adhesive.

Experimental

The carboxymethylation reaction is believed to take place through the intermediate formation of alkali cellulose. With the impure jute, the process would apparently be somewhat more complex because the separation of lignin (by the action of ethyl alcohol and/or chloroacetic acid) *in situ* would have to precede the basic reaction.

Middle portions of jute fibre was selected and finely powdered in a pulverizer, and the powder used as the stock sample. For each experiment, a desired quantity of jute powder was steeped at room temperature for 1-2 hours in a solution of a known concentration of sodium hydroxide in aqueous ethanol (so that the water/cellulose ratio remains at a predetermined value). After the steeping process, instead of squeezing off the mother liquor and treating the soda cellulose with chloroacetic acid, an alcoholic solution of chloroacetic acid was slowly added to the entire mass. This was then maintained at the desired temperature for a period of time with occasional stirring to facilitate the reaction. The product was washed with 80% ethyl alcohol and dried. The crude residue thus obtained was of golden yellow colour and contained about 1-2% lignin. This, when dissolved with sufficient water to make a 2% solution, left a residual by-product, while the sodium carboxymethylcellulose went into solution. After repeated filtration, pure sodium carboxymethylcellulose was precipitated with 80-90% ethyl alcohol. This was separated and carefully dried to obtain the pure sodium carboxymethylcellulose. It was noted that for obtaining satisfactory product, careful control of operating conditions was essential.

Results and Discussion

The degree of substitution in carboxymethylcellulose, as in several other cellulose derivatives, depends to a great extent on the activation of the cellulose. This activation takes place through the alkali used, and the concentration of alkali is believed to play an important role. Other factors, particularly the presence of organic alcohols, have also been found to be of great significance. For example, with purified jute cellulose it was found that while with aqueous sodium hydroxide a concentration of 70% was necessary

to produce a D.S. of 1.05, in ethyl alcohol-water medium a D.S. of about 1.30 could be obtained with only 17% NaOH concentration.

While working with the crude jute, the influence of alkali should be more significant, because it will have effect on the lignin. Results of a series of experiments carried out with varying concentrations of NaOH (10-35%) are presented in Table 1. In these experiments powdered jute

TABLE 1.—DIRECT CARBOXYMETHYLATION OF JUTE CELLULOSE: EFFECT OF ALKALI CONCENTRATION AND WATER/CELLULOSE RATIO.

Concentration of alkali (%)	Water/cellulose w/v ratio	Yield (g)	Degree of substitution	Solubility in water
10	1.0	—	0.07	Insoluble
13	1.0	2.0	1.10	Soluble
15	1.0	2.0	1.17	„
17	1.0	2.5	1.25	„
20	1.0	2.5	1.26	„
35	2.0	2.0	1.20	„

Jute taken for each experiment = 5.0 g; Cl. CH₂.COOH taken = 8 g in 10 ml. EtOH
 Water = 5 ml; EtOH = 30 ml; steeping time = 1½ hours.
 Temperature for carboxymethylation = 40-45°C.
 Time for carboxymethylation = 5 hours.

cellulose was steeped in a definite volume of EtOH-H₂O mixture containing varying amounts of NaOH for different experiments; this was followed by the addition of a solution of Cl. CH₂.COOH in ethyl alcohol and carboxymethylation continued at 40-45°C for five hours. It will be seen that no effective carboxymethylation took place if the NaOH concentration was 10% or less. The carboxymethylation increased sharply between this and 13% NaOH and a D.S. of 1.10 was obtained; beyond this concentration, the D.S. increased slowly and reached a maximum (between 17 and 20% alkali concentration) of about 1.25. With the higher concentration (35%) of the alkali, the D.S. was somewhat lower; but this is explained to be due to the effect of higher proportion of water used (water/cellulose ratio = 2.0) to avoid the formation of (otherwise) immiscible layer.

The variation of D.S. with the concentration of the alkali observed in this present investigation is basically similar to that found, earlier with purified jute cellulose. This suggests that the alkali used here did not, to any great extent, go to solubilize the lignin (in the crude jute). As the

final product was freed from most of the lignin, the latter must have reacted with ethanol and chloroacetic acid.³

The Progress of Carboxymethylation with Time.—In all the preceding experiments the products after carboxymethylation were left aside for twenty four hours in the hope that the process might proceed slowly during this period and relatively higher D.S. values would be obtained. As the time factor is important in commercial practices, it was considered important to determine the nature of the benefit derived from this. Results of two parallel sets of experiments were carried out keeping all other variables the same, but in one the products were further processed immediately after the period of carboxymethylation was over, while in the other the product in each was left aside for twenty four hours before further processing (Table 2).

TABLE 2.—PROGRESS OF DIRECT CARBOXYMETHYLATION OF JUTE CELLULOSE IN WATER-ETOH, WITH TIME.

Duration of carboxymethylation hours	Properties of the products obtained after an overnight stay		Properties of the product obtained without overnight stay	
	D.S.	Solubility in water	D.S.	Solubility in water
0.33	—	—	0.55	Not good
0.66	0.61	Not good	0.80	Soluble
1.00	0.60	„	0.84	„
2.00	0.77	Soluble	0.96	„
3.00	0.99	„	1.26	„
4.00	1.10	„	1.23	„
6.00	1.11	„	1.24	„
10.00	1.20	„	1.34	„

Concentration of NaOH used = 17%
 Other conditions were the same as described under Table 1.

The effect can be clearly noted, as well as that of the duration of carboxymethylation itself from Fig. 1. Under the experimental conditions, the substitution apparently starts from the beginning and proceeds rapidly upto four hours, after which it slows down. If the product is kept for a long time, some hydrolysis (or other side reactions) sets in so that the D.S. of the product decreases to some extent. It is considered optimum to continue the carboxymethylation for 4-5 hours and then further process the products soon afterwards.

The solubility of the sodium salt appears to be dependent on the D.S. rather than any other experimental variable.

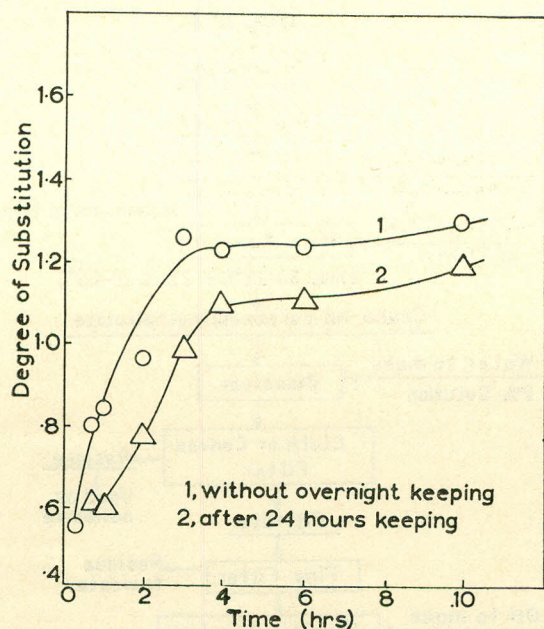


Fig. 1.— Variation of D. S. with period of direct carboxymethylation of jute in EtOH.

The Effect of Temperature of Carboxymethylation.— In the foregoing experiments steeping of cellulose in alkali was carried out at 28-30°C and carboxymethylation at 40-45°C. This temperature was noted to yield the highest D.S. with purified jute cellulose. In order to establish the optimum temperature range for carboxymethylation of the crude jute, a wider range, *viz.*, 50-60°C was investigated. Results are given in Table 3.

TABLE 3.—EFFECT OF TEMPERATURE ON DIRECT CARBOXYMETHYLATION OF IMPURE JUTE.

Carboxymethylation temperature °C	Amount of product (g)		Degree of substitution	Solubility in water
	Crude	Pure		
5	6.0	—	0.11*	Insoluble
10	6.8	—	0.30*	Somewhat dispersible
20	9.0	2.2	0.86	Soluble
30	11.5	3.0	1.48	"
40	11.0	2.8	1.43	"
45	11.0	2.8	1.40	"
60	9.0	2.3	0.85	"

*D.S. refers to crude products.

At low temperatures (below 10°C), the reaction was slow; the D.S. of the product was low, so much so that the crude product could not be further purified. Between 10° and 30°C, the extent of carboxymethylation varied steadily with temperature and reached more or less a maximum value at the latter temperature. Between 30° and 40°C (see Fig. 2), the D.S. did not change very

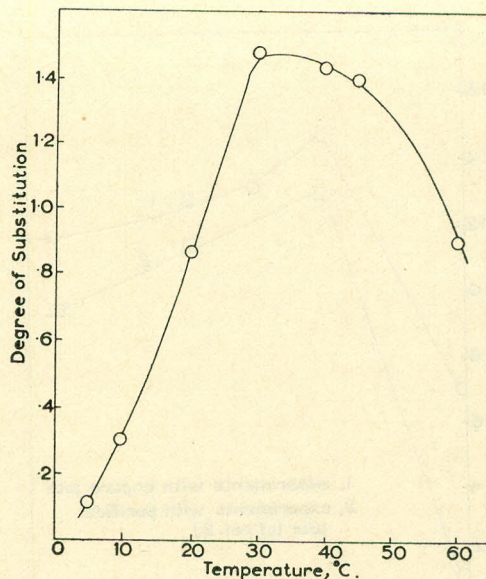


Fig. 2.— Effect of temperature on the carboxymethylation of jute in EtOH.

much; but beyond 40°C, it dropped sharply. Thus, temperature was shown to be a very important variable in the process. The mechanism responsible for lower substitution at higher temperature is not yet fully understood. The range of temperature of 30-35°C was considered optimum. For handling larger quantities of raw materials, it was considered more desirable to carry the reaction initially at 30-35°C, and then raise it to 40-45°C for more or less an equal period of time.

The Effect of the Variation of Water/Cellulose Ratio.— It had earlier been seen with purified jute cellulose that use of EtOH-H₂O as reaction medium had definite advantage over carboxymethylation in aqueous medium; moreover the proportion of water to cellulose had also an important bearing on the substitution. Experiments with impure jute has again confirmed the earlier observation of the effect of water/cellulose ratio.

In the present series, the effect of water/cellulose ratio was studied by changing the quantity of water (and ethanol) but keeping other factors at those points found optimum in the earlier section. The carboxymethylation was carried out for two hours at 30-35°C, followed by another two hours at 40-45°C. The variation of the D.S. with the water/cellulose ratio is shown in Fig. 3.

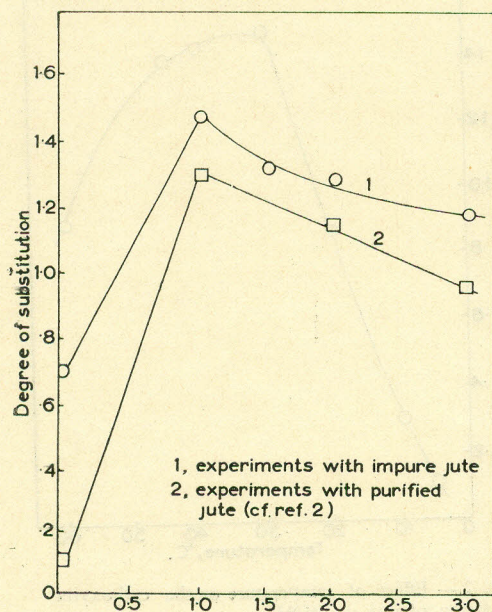


Fig. 3.— Effect of water/cellulose ratio on degree of substitution of product.

For comparison, the results of similar experiments carried out with purified jute cellulose in ethanol-water medium are also shown. Interestingly enough the general trend of the curves is similar—the D.S. increased with increasing water/cellulose ratio and showed a maximum for a ratio of 1.0, after which it again decreased. But there are two points of difference. First, in complete absence of water, the impure jute gives a relatively higher D.S. than with purified jute; and secondly, with crude jute the maximum is considerably higher and the effect of further increases in the proportion of water less pronounced. This may be explained by considering that in the presence of ethanol/chloroacetic acid while the lignin is solubilised, the cellulose is available in a more reactive state.

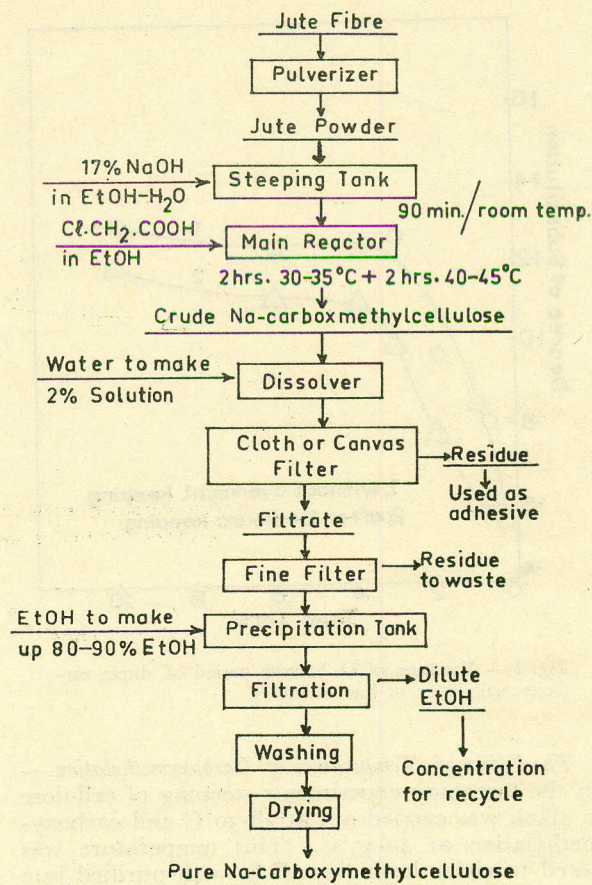


Fig. 4.— Final flow sheet for the preparation of pure Na-carboxymethylcellulose from (impure) jute.

It has thus been found that with impure jute the pure Na-carboxymethylcellulose may be prepared just as well as with purified cellulose; and under optimum conditions, a higher degree of substitution (1.48) may be obtained. Considering all factors, a flowsheet as presented in Fig. 4 has been drawn out to represent the process.

References

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