

STUDIES ON CARBOXYMETHYLCELLULOSE

Part IV.—Effect of Pressure Pretreatment

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By effecting the major part of the alkali treatment under pressure, better substitution may be obtained in carboxymethylation of jute cellulose. The time factor for pressure treatment is important and the optimum was found to be 4 hours. Thus, with impure jute, the highest value for degree of substitution obtained was 1.60.

Introduction

Carboxymethylation is usually carried out commercially with cotton linters or quality wood pulp in aqueous medium. The products thus obtained are reported to possess a degree of substitution not exceeding 0.80, and largely used as a detergent aid. In this laboratory, a systematic study is being carried out on the process of carboxymethylation with particular reference to jute. It was first observed¹ that in aqueous medium, carefully purified jute cellulose responded better towards carboxymethylation than cotton, but for a relatively high degree of substitution (ca. 1.05), an alkali concentration of 50-70% was required. It was further observed that with this degree of substitution the product developed an ability to form stable oil-water emulsions.

Later it was noted² that by conducting the carboxymethylation in water-ethanol mixture, much better results were obtained with purified jute cellulose (D.S. of upto 1.30). This result was interesting, and a tentative mechanism of this reaction was also suggested. Subsequently, it was observed³ that better results (D.S. 1.48) could be obtained by starting impure jute (i.e. without prior removal of lignin) and this was explained by supposing that ethanol and chloroacetic acid, while causing the delignification, left the cellulose in a relatively more reactive state, which was probably responsible for the better carboxymethylation in the subsequent step.

During the course of the above studies it was thought that the soda cellulose formation plays a significant role in the overall reaction. In the present investigation therefore, the major part of the first step of alkali treatment was carried out under pressure. In order that the effect of such pressure treatment may be better understood, subsequent carboxymethylation was carried out with all the above conditions, viz. in aqueous medium with purified cellulose, in organic solvent medium with purified jute and in organic solvent medium with impure jute. It was noted that with

pressure alkali treatment, better results were obtained in all cases and a maximum D.S. of 1.60 has been obtained with impure jute in single treatment.

Experimental

Jute fibre, after discarding the top-most and lowermost portions, was cut into sizes of about 1 in. It was then finally powdered in a shredder. The impure jute was used either as such or delignified.

For delignification, the powdered jute was first boiled for 20-30 min with 1% NaOH. After filtering and washing thoroughly with water, the main bulk of the adhering water was squeezed out and the moist powder treated with chlorine gas for about 1 hr when the colour changed to golden yellow. This was then washed twice with distilled water and then boiled with excess of 2% sodium sulphite solution and subsequently made alkaline and boiled for 5 min. It was then washed well on cloth filter. (If the cellulose thus obtained still retained some lignin, a second chlorination treatment was given.)

In the early experiments attempts were made to combine both the steps (conversion to alkali cellulose and carboxymethylation) and carry them simultaneously in the autoclave; but this was unsatisfactory. The product was somewhat charred and separation of the Na carboxymethylcellulose was difficult.

In the final procedure adopted, the impure or purified jute powder as described above, was steeped with the reagent for 1½ hr in the open and then for 4 hr in an autoclave. The autoclave was then allowed to cool down after which the carboxymethylation was carried out in the usual way as described in earlier papers. The degree of substitution was determined by the uranyl gravimetric method.⁴

The product obtained from impure jute was of a golden yellow colour and contained a little lignin.

This was dissolved to make a 2% aqueous solution and after filtering off the residue, pure Na carboxymethylcellulose was reprecipitated by ethanol treatment. The D.S. reported in all the above cases are those for purified products.

Results and Discussions

Carboxymethylation of cellulose is believed to take place through the intermediate formation of alkali cellulose. Although it is not yet clearly understood whether with concentrated alkali cellulose forms a cellulose or simply an adsorption complex, some activation of the reactive groups (hydroxy groups) appear to take place and this helps the subsequent reaction. It is also known that accessibility of reagent to the crystalline regions of the cellulose structure plays an important role in its reactions. It was therefore believed that the application of pressure may effect a wider distribution (penetration) of the alkali and facilitate the soda cellulose formation further.

The first set of experiments (A₁-A₅, Table 1) was carried out with purified jute cellulose in aqueous medium using 70% NaOH. For comparison one experiment was carried out in the open (i.e. at 1 atm pressure). In others, in different experiments, the pressure was varied up to 4

atm. Application of pressure had a remarkable effect (cf. Fig. 1) on subsequent carboxymethylation as depicted by the degree of substitution of the product. Without application of pressure, the degree of substitution of the product was only 1.05. This increased sharply to 1.14 by increasing the pressure to 2.0 atm. Further increase of pressure has but very little effect (D.S. increasing to 1.16 by increasing the pressure to 4.0 atm). It appears therefore that under the present experimental conditions, there is a limit to which the OH groups may be activated.

The second set of experiments (B₁-B₅, Table 1) was carried out with purified jute cellulose; but both alkali treatment as well as the carboxymethylation was carried out in aqueous ethanol in proportions found optimum in earlier experiments² (water-ethanol ratio of 1:6 and water-cellulose ratio of 1:1). The variation of D.S. with change of pressure treatment can be seen on a comparative basis from Fig. 1. Two important observations emerge from these experiments first that the D.S. of the products are generally higher than those obtained from the corresponding experiment in aqueous medium, even though in the latter case a much stronger alkali solution was used; and secondly that the increase of D.S. with increase

TABLE 1.—CARBOXYMETHYLATION OF JUTE (CELLULOSE) UNDER DIFFERENT CONDITIONS. EFFECT OF ALKALI TREATMENT UNDER PRESSURE.

Expt. No.	Raw material and reagents	Temperature in autoclave °C	Pressure in autoclave (atm)	Degree of substitution	
A ₁	10g purified jute cellulose, 35 g NaOH, 50 ml H ₂ O	—	1.0	1.05	
A ₂		120-125	1.00-1.25	1.10	
A ₃		130-135	1.80-2.00	1.14	
A ₄		140-145	2.70-2.75	1.15	
A ₅		150-155	3.80-4.00	1.16	
B ₁	10 g purified jute cellulose, 12 g NaOH, 10 ml H ₂ O	+60 ml EtOH +20 ml EtOH	—	1.0	1.17
B ₂		120-125	1.00-1.25	1.22	
B ₃		130-135	1.80-2.00	1.38	
B ₄		140-145	2.70-2.75	1.39	
B ₅		150-155	3.80-4.00	1.40	
C ₁	10 g impure jute, 12 g NaOH, 10 ml H ₂ O + 60 ml EtOH	+20 ml EtOH	—	1.0	1.40
C ₂		120-125	1.00-1.25	1.41	
C ₃		130-135	1.80-2.00	1.51	
C ₄		140-145	2.70-2.75	1.59	
C ₅		150-155	3.80-4.00	1.61	

Steeping time=1½ hr at room temp + 4 hr under pressure.

ClCH₂COOH taken=16 g; temp of carboxymethylation=40-45°C; duration of carboxymethylation=5 hr.

of pressure from 1.0 to 2.0 atm was considerably steeper in this case. It is also interesting that further increase of pressure beyond 2.0 atm does not have any effect on the overall process. Under these experimental conditions, the highest D.S. value noted in the product was nearly 1.40.

The third set of experiments was carried out with impure jute powder (i.e. without prior delignification). As expected the product was somewhat golden-yellowish (crude Na carboxymethylcellulose). This was purified and the results presented (C₁-C₅, Table 1) are those for the pure product. The relative position of the curve for this set of experiments (Fig. 1) again confirms that the highest D.S. of the Na carboxymethylcellulose are obtained with impure jute. But the effect of pressure is somewhat different. Thus while a pressure of 2 atm was sufficient to give the maximum effect in alkali treatment with purified jute, in this case (with impure jute) the D.S. of the product increased steadily upto about 3 atm after which, of course, it remained more or less steady. The slope of the curve was also relatively less in this case. The highest D.S. value obtained with impure jute was about 1.60.

Progress of Carboxymethylation with Time.—In all the previous experiments, alkali treatment was carried out for 1½ hr in the open, followed by 4 hr of autoclave treatment. A set of experiments

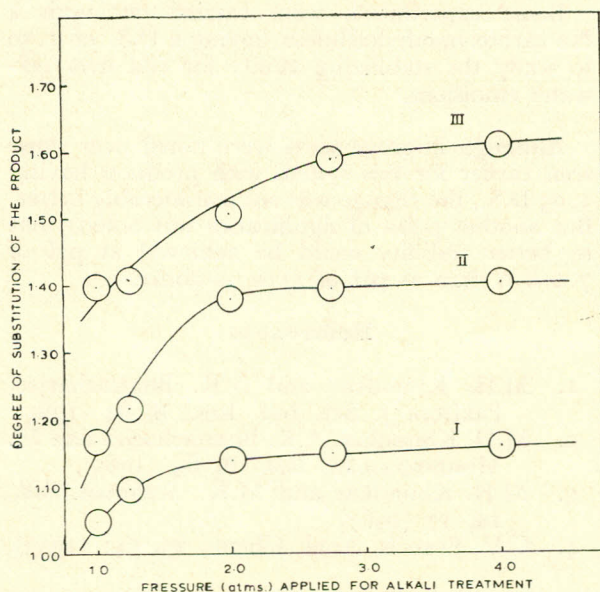


Fig. 1.—Effect of pressure applied for alkali treatment on the degree of substitution of the product. (I, purified jute in aq. medium; II, purified jute in ethanol medium; III, impure jute in ethanol medium).

was now carried out with impure jute in which other conditions were kept the same (jute, 10 g, water 10 ml, ethyl alcohol 60 ml, steeping 1½ hr at 29–30°C followed by autoclave treatment at 2 atm, monochloroacetic acid 16 g in 20 ml ethyl alcohol treated at 40–45°C for 5 hr), but the duration of autoclave treatment was varied from 1 to 5 hr in separate experiments. Variation of D.S. of the product with time of pressure treatment is shown by the curve in Fig. 2. The results are strikingly significant. The D.S. increases steadily with time of autoclave treatment—relatively sluggish upto 2–3 hr, but rather sharp after that up to 4 hr. Surprisingly there is no further substitution beyond this period of autoclave treatment. Thus with 1 hr of pressure treatment the product obtained had a D.S. of 0.95; the corresponding values for 3 and 4 hr are 1.11 and 1.51. It was thus clear that the duration of pressure treatment was clearly a more significant factor. From this it probably follows that the carboxymethylation is directly dependent on the interaction of alkali with cellulose, and the latter reaction is not instantaneous but proceeds with time, even under the influence of pressure.

Final Flow-sheet.—On the basis of the results obtained above, the flowsheet of the process may be worked out as in the chart at next page.

Water Solubility and Emulsifying Properties of the Product.—The various uses of Na carboxymethylcellulose depend to a great extent on its solubility in water. This, in turn, should depend on the

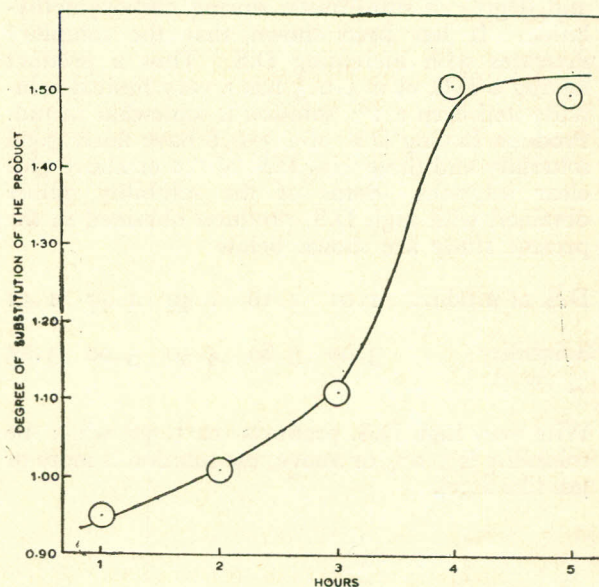
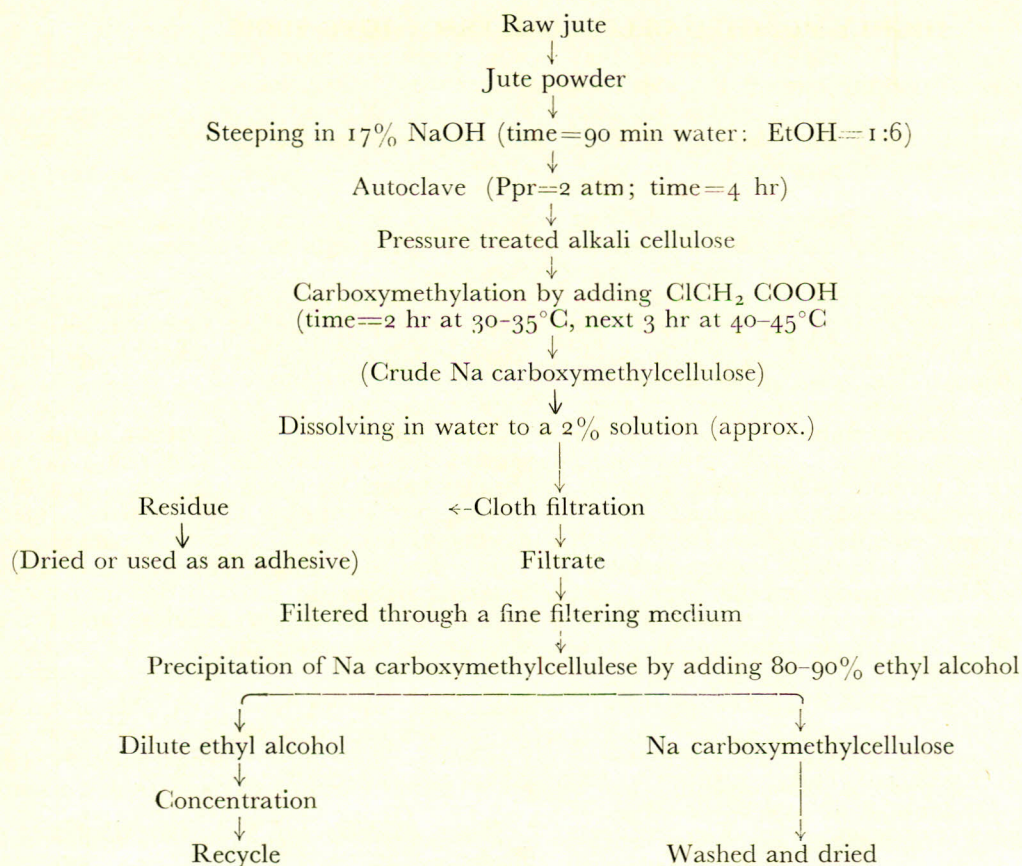


Fig. 2.—Duration of alkali treatment under pressure.



method of preparation, particularly on its (method) influence on the shortening of the chain length and degree of substitution during carboxymethylation. It has been shown that the solubility increases with increasing D.S. Thus a product having a D.S. of 0.4-0.5 has a very limited solubility and even a 1% solution is somewhat turbid. Products having D.S. of 0.7-0.8 have fairly good solubility and those with D.S. of 1.0 or above give clear solutions. Some of the solubility values obtained with high D.S. products obtained in the present study are shown below:

D.S. of product	1.01	1.18	1.40	1.47	1.51
Solubility % (w/v)	3.00	3.60	4.50	5.00	5.25

With very high D.S. products (ca 1.50) when the solubility is 5.0% or above, the solution is more or less like a gel.

Some experiments were carried out with a Na carboxymethylcellulose having a D.S. of 1.50 to study the stabilizing ability for cod liver oil-water emulsions.

Although improvements were noted over those seen earlier for this system with products having 1.05 D.S., the change was not considerably better. But another point of significance was noted; that is, better stability could be achieved at pH of 7.0-8.0 than at pH of 11.0 or above.

References

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