

Two-Step Synthesis and Characterization of Carboxymethylcellulose from Rayon Grade Wood Pulp and Cotton Linter

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Summary: Carboxymethylcellulose (CMC) was prepared from bleached cellulose pulps obtained from the wood of *Eucalyptus globulus* (Eup), *Picea smithiana* (Picp) and cotton linter pulp (CLP), which are used for viscose rayon fiber. The chemical composition of cellulose pulps (alpha-cellulose, hemicellulose, moisture, ash, intrinsic viscosity and color brightness) was also determined. The dried cellulose was alkalinized using 40 % NaOH at 25 °C for 1.5 hour. Sodium monochloroacetic acid (MCA) from 5-7 g per 5 g cellulose was added to the slurry and the temperature was adjusted to 55 °C for 3.5 h. The pulps carboxymethylated by one successive reaction step, were again etherified, using monochloroacetic acid as an etherifying agent and isopropyl alcohol as a solvent. The best result of etherification was obtained in the case of cotton linter pulp. The degree of substitution (DS) of CMC was found to be dependent upon the source of cellulose, but generally it was high in the case of cotton linter pulp. The second etherification reaction step increased the DS up to 1.9, by increasing the concentration of MCA, which in turn improved the CMC solubility in water. Qualitative and quantitative analysis of CMC were carried out to determine the moisture, ash, sodium chloride, degree of substitution, purity and viscosity of carboxymethylcellulose. This investigation helped to find the proper conditions for the etherification of rayon grade pulps and showed that high quality CMC can be prepared from cotton linter pulp by two consecutive etherification reactions.

Introduction

Carboxymethylcellulose (CMC) is the most important commercial cellulose ether. It is an anionic polyelectrolyte prepared by the reaction of cellulose with monochloroacetic acid (MCA) in the presence of sodium hydroxide (NaOH). In practice, the manufacture of CMC involves two steps.

In the first step, the cellulose is treated with NaOH, often in the presence of inert solvent, which acts both as a swelling agent and as a dilutant and thus facilitates good penetration of NaOH into the cellulose structure. The cellulose-NaOH activation reaction is often referred to as mercerization and it is generally performed at room temperature. The temperature conditions used during mercerization have a significant impact on the properties of the end product, *i.e.* on the CMC quality. The alkali cellulose is accessible and reactive toward MCA, which is added to the reaction in the second step. The reaction between alkali cellulose and the etherification agent is normally carried out at about 70 °C in the aqueous system. At the same time, NaOH reacts with MCA to form sodium glycolate and sodium chloride, *i.e.* in dissolved form [1].

The CMC can be neutralized and dried immediately to give a technical grade or neutralized and washed to give a purified grade. Purified grades for industrial applications often have a purity of about at least 98 %, while CMC grades for food, pharmaceuticals and personal care applications have a purity of at least 99.5 % [2].

The sodium form of carboxymethylcellulose is commonly known as CMC, but food grade is also known as cellulose gum. CMC is sold as a white to off-white powder and is available in several grades, in a variety of types depending on the degree of substitution (DS), viscosity and particle size [3]. There is a wide array of commercial uses for CMC due to its particular properties. CMC is soluble in water when the degree of substitution is higher than 0.5, giving high viscosity in dilute solutions. The DS is one of the most important properties of CMC. It not only influences the solubility of CMC molecules but also affects the solution characteristics. By definition, the DS is the average number of carboxymethyl groups per anhydroglucose unit (AGU). The theoretical maximum value for the DS is

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3. The DS range for commercially available CMC is generally 0.5-1.5. It has thickening effect, film-forming ability and excellent behavior as a protecting colloid and adhesive [4-5].

Substitution of OH group, for carboxymethyl cellulose occurs mainly at the position C₆. The structure of Na-CM-cellulose, prepared via solid – phase low modulus method is identical to that prepared via a different method. Correlation establishes between spectral characteristics of Na-CM-cellulose and degree of substitution, which can be used for the determination of industrial samples [6]. Effect of temperature, duration of alkali treatment and amount of monochloroacetic acid, have a significant effect on solubility in water, viscosity and content of carboxy-methyl group in the carboxymethylated product [7].

CMC is non-toxic and it is currently finding an increasing number of applications in pharmaceutical, medical and food industries. It is a key component in controlled drug-release pills and in the manufacture of personal care products [8]. It is also used in gels applied as protecting agent during heart, thorax and cornea surgery [9-10].

Most of the CMC applications are based on its rheological properties. The ability of CMC to function as a thickener or flow – controlled agent depends largely not only on its degree of substitution and on the molecular weight, but also on the stiffness of the cellulosic backbone. Cellulose food stock for the production of CMC and other dissolving pulps are currently obtained from bleached pre-hydrolyzed Kraft and acid sulfite pulps or directly from cotton linter. These pulps normally have a high degree of polymerization. However, the use of different raw materials for the preparation of cellulose derivative such as non-wood pulps is a potential source of cellulose that may meet the quality specification required to synthesize some of these derivatives [11].

Baggase, the by-product of sugarcane industry, was used the first time to prepare the Na-salt of CM-cellulose. Carboxymethylation of baggase was studied in detail under various reaction conditions. The emulsifying properties of the purified Na-CMC were studied using olive oil and coconut oil [12]. The objectives of this work were to prepare sodium carboxymethylcellulose (CMC) with different degree of substitution from cotton cellulose in comparison with the characteristics of Na-CMC pre-pared from wood cellulose and to evaluate their physico-chemical properties as a potential material for food and textile industries. Pakistan imports CMC from different countries, which is a great burden on our foreign exchequer. Therefore, there is a need to produce CMC from locally available cheap raw material, such as cotton linter, economically on a large scale.

Results and Discussion

Table 1 shows the chemical composition of the rayon grade pulps used for the synthesis of carboxymethylcellulose. The α -cellulose content for CLP (96.2 %) and Picp (93.7 %) was higher than 90 % required for good quality CMC, while in case of Eup pulp, α -cellulose content was (89.83 %). The high pulp purity is required for the production of cellulose derivatives and the α -cellulose content should be greater than 90 %. Lower α -cellulose content implies the presence of low molecular oligosaccharides, which may affect the yield and quality of the derivative [3].

High content of hemicelluloses and ash was found in wood species of Eup and Picp pulp, while it was the lowest in the case of CLP pulp. Infrared spectroscopy spectra of standard CMC sample with DS of 1.50 and for prepared CLP CMC with DS of 1.9, are shown in Figs. 1, 2 and 3 respectively. The peaks at wave number 1620.1 and 1423.4 cm⁻¹ indicated the presence of carboxymethyl substituent.

Table-1: Chemical composition of the rayon grade pulp

No	Determination	Pulp sample	<i>Eucalyptus globules</i> pulp (Eup)	<i>Picea smithiana</i> pulp (Picp)	Cotton linter pulp (CLP)
1	α -cellulose%		89.83±0.71	93.7±0.21	96.2±0.30
2	Hemi cellulose%		4.44±0.088	5.80±0.085	3.5±0.328
3	Moisture%		5.84±0.064	6.40±0.204	4.83±0.155
4	Ash%		0.12±0.03	0.03±0.015	0.08±0.03
5	Intrinsic viscosity (ml/g)		625±6.23	915±9.07	870±8.01
6	Brightness%		91.0±0.58	87.40±1.15	92.7±0.62

Values are \pm S.D of three determinations in each case.

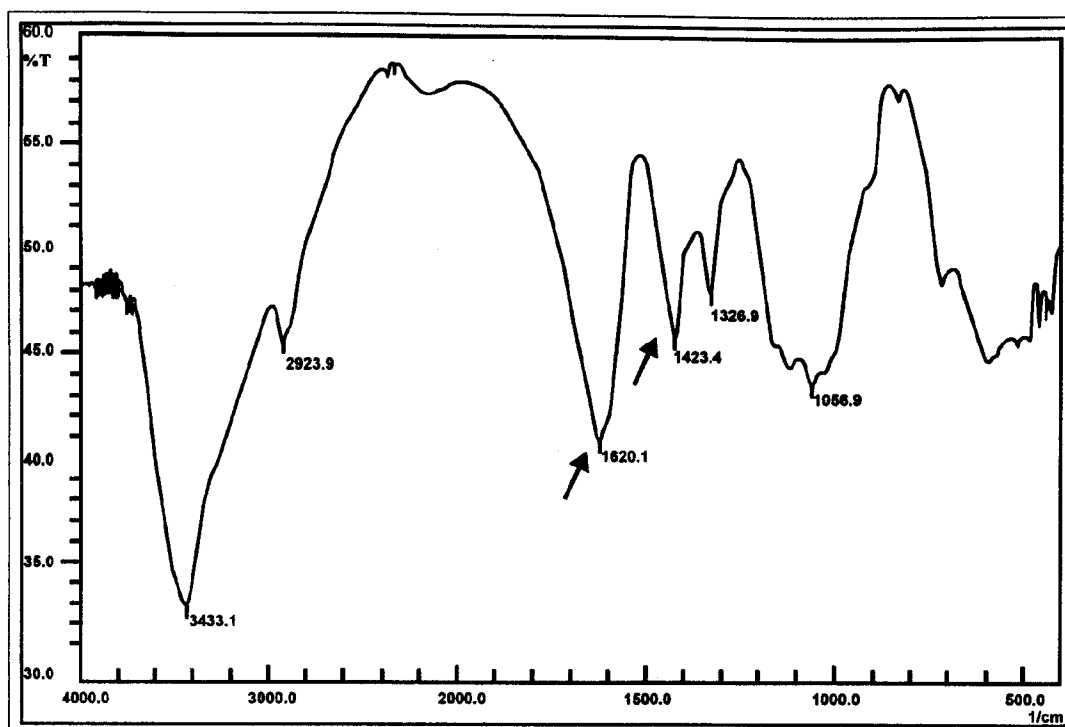


Fig. 1: FTIR-spectra of commercial CMC (German) with DS of 1.5 (Carboxymethyl groups substituent are indicated by arrow).

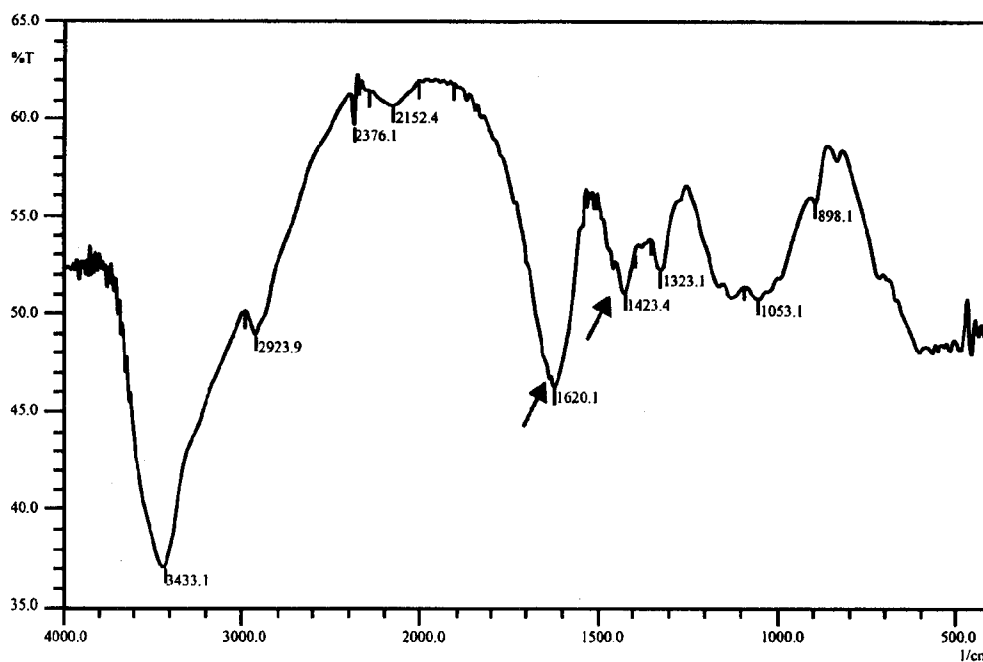


Fig. 2: FTIR-spectra of CMC made from cotton linter pulp with DS of 1.9 which was synthesized using 40 % NaOH and 7g of MCA (Carboxymethyl groups substituent are indicated by arrow).

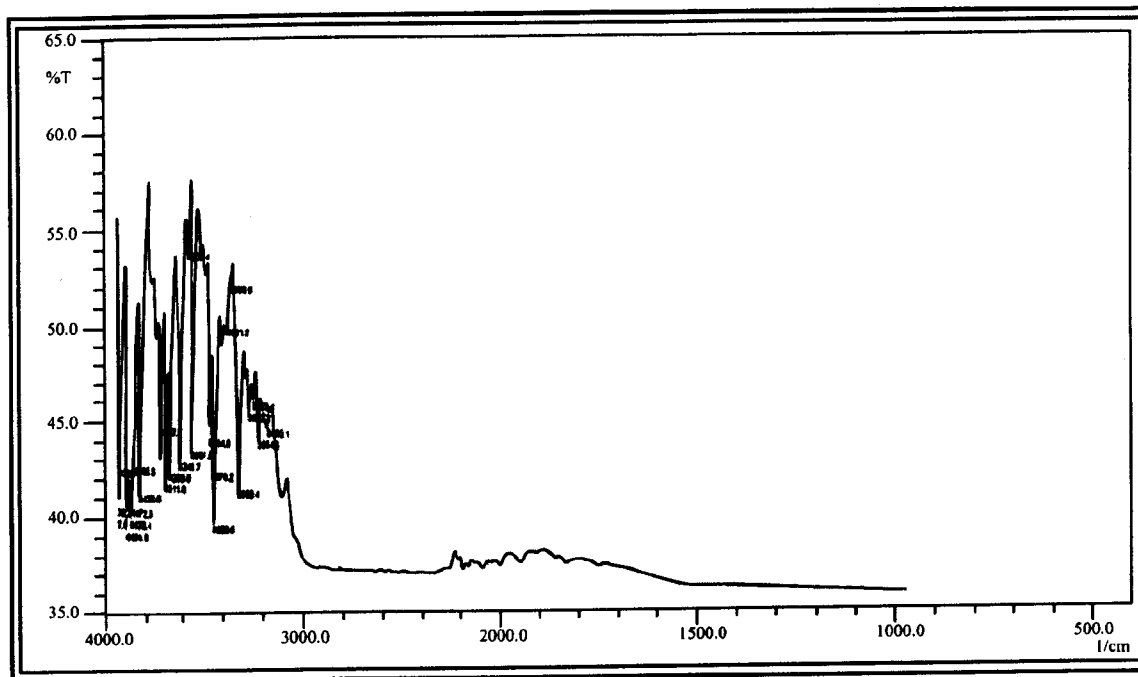


Fig. 3: FTIR-spectra of cotton cellulose pulp without etherification.

According to Pecsok, Shields, Cairns and McWilliam, carboxyl groups as its salts have a wave number about $1600\text{-}1640\text{ cm}^{-1}$ and $1400\text{-}1450\text{ cm}^{-1}$ [13].

The spectra in Fig. 1 are similar to those shown in Fig. 2. The similarity of Fig. 1 and 2 showed that CMC was synthesized from cellulose polymers. Fig. 3 showed that no peak was observed at wave number $1600\text{-}1450\text{ cm}^{-1}$, before the etherification of CLP pulp. Fig. 3 showed transmission bands at wave number $3700\text{-}3140\text{ cm}^{-1}$, which corresponded to the hydroxyl group of anhydroglucose units of cellulose.

The main step in the carboxymethylcellulose reaction is the formation of alkali cellulose, which modified the crystalline structure and increased its accessibility to chemicals by swelling. Cellulose can be swollen in concentrated NaOH, but not dissolved. However, hemicelluloses are extracted from cellulose by alkali treatment.

The amount of hemicelluloses content ranging from 3.5 % - 5.8 % was observed in all these rayon grade pulp samples. The intrinsic viscosity of the

pulps was 625 ml/ g, 870 ml/ g and 915 ml/ g) for Eup, CLP and Picp, respectively. The intrinsic viscosity affects the quality of the CMC. If the intrinsic viscosity of pulp is lower, then the degree of polymerization of pulp will also be lower, finally affecting the viscosity of the final product.

In the preparation of cellulose derivatives, a high solution viscosity is often the decisive quality criterion. It is important to control the final viscosity of cellulose derivatives by using pulp having moderate viscosity ranging from 800-1100 ml/ g [4].

Carboxymethylcellulose prepared from pulps of *eucalyptus*, *picea* and cotton linter was analyzed for purity, degree of substitution, viscosity, moisture and sodium chloride contents. Table-2 shows the degree of substitution of the CMC after two consecutive etherifications. After the first reaction, Eup, Picp and CLP CMCs showed a degree of substitution close to 1, while after the second etherification, the DS values were around 2 for Clp and Pica pulps.

The CMC from Eup pulp had DS of 0.89 and 1.47 after two consecutive etherifications.

Table-2: Characteristics of CMCs after two consecutive etherifications.

No	Pulp Name	Degree of Substitution	Viscosity of CMC (cp)	Purity%	Moisture%	Sodium% Chloride
1	Eup _a	0.74±0.041	578±5.16	95.8±2.06	4.16±0.15	0.62±0.045
2	Picp _a	0.94±0.050	610±8.33	97.1±1.30	4.07±0.25	0.29±0.061
3	CLP _a	1.05±0.061	630±4.57	98.0±0.79	2.56±0.14	0.19±0.025
4	Eup _b	1.47±0.028	645±7.34	96.3±0.68	4.39±0.27	0.48±0.040
5	Picp _b	1.72±0.077	670±8.52	98.2±1.06	3.78±0.23	0.21±0.031
6	CLP _b	1.90±0.082	690±9.11	98.5±1.65	3.05±0.20	0.15±0.026

Values are ± S.D of three determinations in each case.

Where Eup = *Eucalyptus. gobulus* pulp, Picp = *Picea. smithiana* pulp,

CLP = Cotton linter pulp. a= CMC after first etherification reaction

b= CMC after two successive etherification reactions.

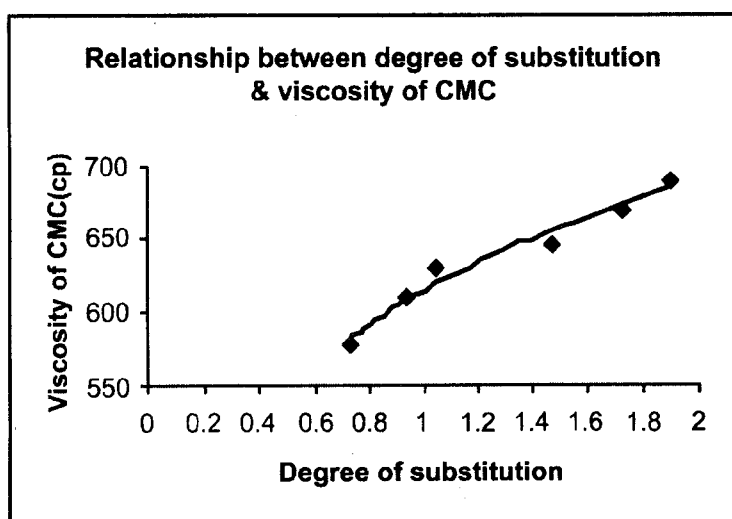


Fig . 4: Relationship between degree of substitution and viscosity of CMC.

The purity of the CMCs was measured after washing the product several times with ethanol (80 %) and absolute methanol, which remove the reaction by-products (NaCl and sodium glycolate). The purity of all CMC preparations was higher than 95 %; after second etherification step, the purity of Picp and CLP pulp was above 98 %, as required for commercial grade CMC.

The viscosity of 1 % carboxymethylcellulose was in the range of 500-695 centipoises. The viscosity of first etherification was low, while for second etherification, it was higher due to availability of remaining position on cellulose chain for further etherification and due to a slight increase in the concentration of MCA (7 g/ 5 g cellulose sample).

It is obvious that at the same level of NaOH concentration, with increasing level of MCA

increased viscosity of the CMC, which was in accordance with the work of Heinz [14].

There is a direct relationship between viscosity and the degree of substitution of the CMC as represented in Fig. 4. For instance, the CMC prepared from Eup pulp with one etherification treatment had the lowest DS (0.74).

The effect of increase of DS to raise the viscosity of CMC solution was due to more carboxymethyl groups substituted by the hydroxyl groups of the cellulose polymers. These carboxymethyl groups act as hydrophilic group, therefore an increase of DS thus increased the ability of CMC to immobilize water in a system.

It appears that the properties of the prepared CMC were closely related to the amount of alkali

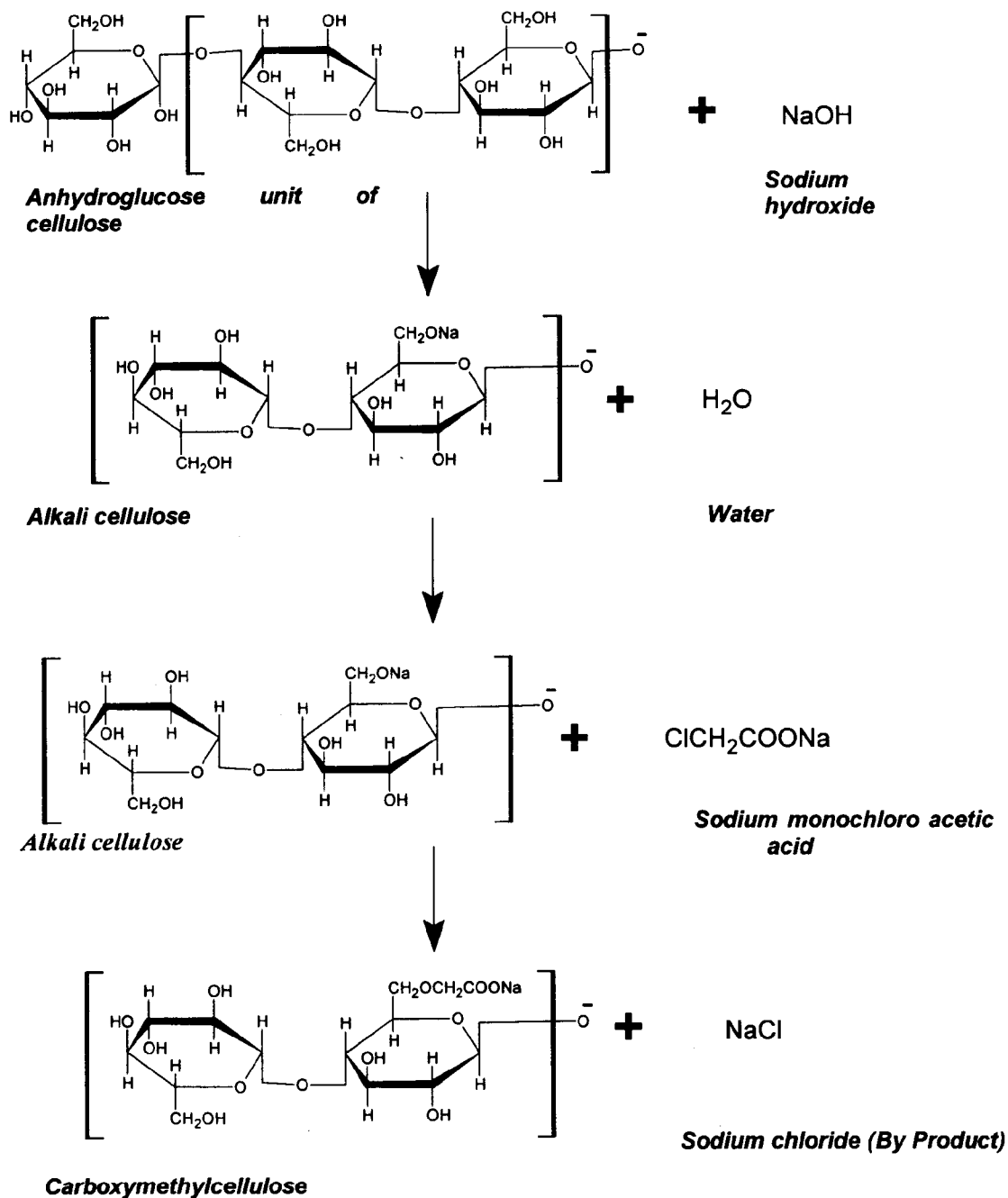


Fig. 5: The reaction for the synthesis of carboxymethylcellulose.

soluble material in the cellulose pulp. The Eup pulps were the most difficult to etherify and the CMCs that were obtained had low purity value than those of the other cellulose pulp. The low purity of the CMCs prepared from Eup pulps may be due to the high content of alkali-soluble material and low

accessibility of its structure during etherification reaction. The CMC obtained from Clp had high DS and very low content of alkali soluble material.

The CMC purity increased with increasing DS. This phenomenon suggests at a higher DS, more

MCA molecules are substituted to the cellulose polymer, thus decreasing the possibility of MCA to react with NaOH to form by-products [15].

The results showed that Picp and CLP pulps are suitable to prepare cellulose derivatives such as CMC. Cotton linter contains high α -cellulose content and it is easily available and a very cheap raw material for the synthesis of CMC. Both Picp and CLP pulp have moderate viscosity so they can be used as thickening agents in the textile finishing operation.

Experimental

Pulp Composition

Three rayon grade pulp samples of *Eucalyptus globulus*, *Picea smithiana* and cotton linter pulp were provided by Chemi Visco Fiber (Nawabshah). For CMCs synthesis, following chemicals were used: Isopropanol (99.5 % - Merck), Sodium hydroxide (98 % -BDH), Monochloroacetic acid (99 % - BDH), Acetic acid (99.99 % - Merck), Perchloric acid (71 % - BDH), Ethanol (99.5 % - Merck) 1,4-Dioxane (99 % - BDH), Methanol (99.8 %-Merck), Ferrous ammonium sulphate (99 %-Merck), Ammonia (28-35 %-Aldrich), Copper sulphate (98 % - Merck) and Silver nitrate (99.99 % - Merck).

The ash content was determined by igniting the sample of pulp at 580-600 °C in a muffle furnace (Swiftech, K.E-671) [16]. Moisture content was analyzed at 105 °C in drying oven (Heraus, OVG-220-010D) for two hours [17].

For the determination of alpha-cellulose and hemicellulose content, standard testing method of TAPPI-203-cm-99 (Technical Association of Pulp and Paper Industry), was used. 1g sample of oven dry pulp was taken in a weighing bottle and transferred into a 250 ml beaker, followed by maceration of the shredded sample of pulp with 40 ml of 18 % NaOH solution at 20 °C. After 30 minutes, additional mercerization was carried out in a water bath at 20 °C, followed by the addition of 75 ml of distilled water to the alkali cellulose mixture with continuous stirring. The content of the beaker was filtered immediately by means of Gooch crucible. The residue was then washed in the Gooch crucible with 40ml of 10 % acetic acid and allowed to soak for 5 minutes. Then, the alpha-cellulose was washed with water until all the acid was cleared and alphacellulose

was then determined gravimetrically. Hemicellulose was soluble in 18 % NaOH solution and determined in the residue filtrate by titrating with 0.1N ferrous ammonium sulfate standard solution [18].

Intrinsic viscosity of pulp samples was determined by using the capillary viscometer. The oven dry pulp samples were dissolved in cuprammonium solution, having the Cu concentration in the range of 14.8-15.2 g/ l and the ammonium concentration being 190-210 g/ l. The calculated weight of oven dry pulp was taken to give 1 % solution and the time of flow of the sample solution was measured and blank results were reported in centipoises and found to be average of at least three tests [19].

Carboxymethylcellulose Synthesis

Carboxymethylcellulose (CMC) was synthesized in a two-step reaction from different types of rayon grade pulps.

CMCs were synthesized following the procedure describe by Browning (1967) for cotton linter. Cellulose was suspended in isopropyl alcohol under mechanical stirring at room temperature and 40 % NaOH was added to the mixture. It was stirred for 90 minute to yield alkali cellulose. 5 g monochloroacetic acid was then slowly added to the mixture for 30 minute and its temperature was maintained at 55 °C for 3.5 hour. After this time, methanol (70 % v/v) was added to the reactor and the mixture was neutralized with acetic acid (90 % v/v). CMC was then recovered by filtration and washed six times with ethanol/water (70/30 v/v). Finally, the product was washed with pure methanol and oven dried at 60 °C [20].

After the first etherification reaction, all the CMCs were submitted to a second reaction to increase the DS. The second etherification treatment was performed at the same condition as the load of chemicals, but only the concentration of the MCA was slightly increased from 5 to 7 g per 5 g of each cellulose sample. Similarly, other rayon grade pulps were also used for the etherification reaction to prepare cellulose ether for commercial utilization.

Characterization of Carboxymethylcellulose

Infrared spectra of the CMC samples were recorded with Shimadzu FTIR-8210 PC. Pellets were

made from CMC samples (2~5 mg) ground with KBR (700~800 mg). Transmission was measured at the wave number range of 4000-400 cm^{-1} .

The prepared CMCs were analyzed for the degree of substitution with a non-aqueous acid base titration. The sample was refluxed with glacial acetic acid and the resulting sodium acetate was titrated with a 0.1 N standard solution of perchloric acid in dioxane to a potentiometric end point. The moisture was determined by placing the samples in dry oven, capable of maintaining a temperature of 105 °C, for calculating the total solids in the sample.

The viscosity of 1 % aqueous solution of carboxymethylcellulose was determined at 25 °C and the viscosity was measured with the Brookfield type viscometer. The amount of sodium carboxymethylcellulose required for desired concentration on a dry basis was calculated from the known moisture content. The purity of crude carboxymethylcellulose was determined by micro filtration of the samples in a pressurized filtering crucible at 60 to 65 °C. The undissolved matter was transferred quantitatively to the crucible, and then dried weighed and calculated as a percentage of sodium carboxymethylcellulose.

The determination of sodium chloride content of carboxymethylcellulose was carried out by dissolving 5g of the CMC sample into 50 ml water and 5ml of H_2O_2 (30 %). Then the beaker was placed on the steam bath for 20 min. The beaker was cooled, 100ml distilled water was added followed by 10ml of Conc. HNO_3 . Further, the mixture was titrated with 0.1N standard solution of silver nitrate to a potentiometric end point. Hydrogen peroxide was added to reduce the viscosity of the solution [21].

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