

## Catalyst-Free Conversion of Alkali Cellulose to Fine Carboxymethyl Cellulose at Mild Conditions

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**Abstract:** Cellulose fibers were converted into a valuable cellulose derivative, which is easily marketable with additional values. Alkali cellulose and carboxymethyl cellulose (CMC) is the most important cellulose derivatives. Alpha-cellulose was furnished as raw material for production of CMC, which is obtained from short cotton fibers, then purified. Alpha-cellulose is available in the international market. Preparation of carboxymethyl cellulose was conducted using sodium hydroxide solution in sequential reactions with monochloroacetate (MCA) at desired condition. Alkali cellulose has been successfully synthesized in a batch reactor with degree of substitution (DS) of 0.15 to 0.7 and excellent purity of 99.3% at pH 7. The maximum degree of substitution of 0.7 was defined with 40% MCA and 30% NaOH. The reaction temperature was controlled and the purity of the product was examined through the course of reactions. The samples of CMC were examined by scanning electron microscope and FTIR techniques. A comparison study with CMC available in the international market has been conducted. The obtained results for the synthesized CMC with more than 99% purity were promising. The synthesized CMC was easily dissolved in water. The obtained product is absolutely recommended for pharmaceutical applications and as food additives.

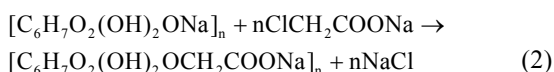
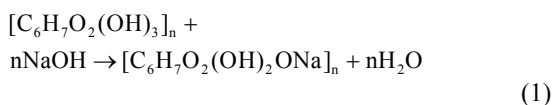
**Key words:** Carboxymethyl cellulose • Alkali cellulose • Ether cellulose • Soluble cellulose derivative • Cellulose

### INTRODUCTION

Depletion of petroleum based products created of interests in cellulose and cellulose derivatives as a renewable resource. Alkali cellulose and carboxymethyl cellulose (CMC) are the most important cellulose derivatives. Cellulose is a linear and high molecular weight polymer as well as natural, renewable, and biodegradable material. Although, due to hydrogen bonds that associated with structure of molecular cellulose, it neither melts nor dissolves readily in common solvents [1, 2]. But its water-soluble derivatives have found various applications [3]. The purified product has major contribution in food, pharmaceutical, detergents and cosmetics industries. It is used as a preservative for coating of fresh fruit and thickener for pharmaceutical products [4-6]. CMC is often used for improvement of

paper quality, as it inter-bonds between cellulose fibers. The film coated on the cellulose fibers by CMC gel has enhanced the physical property of paper for printing purposes [7]. Beside the wide use of CMC, it is used as drilling mud in oil industry [8]. In addition, CMC is applied as a dye thickening in textile industry [9]. CMC as detergent and surfactant are used as anti-dirt agent for protection of fibers surface [10]. CMC has been synthesized from raw cellulose, wood, paper cotton-linter fibers, Lantana camara, banana plants and sugar beet pulp [3, 5, 7, 11-13]. The main step in carboxymethylation reaction is the formation of alkali cellulose, which has modified the crystalline structure of cellulose and increased the accessibility of fibers to chemicals by swelling. Cellulose fibers are swollen in concentrated NaOH [14]. CMC is ether in which the hydroxyl group of anhydrous glucose is replaced by the carboxymethyl

group of MCA. Under alkaline conditions, the hydroxyl group of cellulose shows high activity. For production of CMC, two consecutive steps of reactions are required [7, 15]. These reactions are summarized as basification and etherification as follow:



The above reaction can be carried out with or without solvents [5]. Isopropanol is used as a suitable solvent. The first reaction is endothermic as the second reaction is exothermic, liberates 41.5 Kcal/mol. Therefore, the removal of emitted heat to out of the reaction vessel via a jacket was required. The product is known as sodium carboxymethyl cellulose with molecular weight of 242.4 [3].

The purpose of present research paper was to introduce the synthesis of CMC as a pharmaceutical and food based products. Basification and etherification reactions were successfully carried out using NaOH and MCA, respectively. The degree of substitution of NaOH on cellulose fibers was also investigated. The morphology of the fabricated CMC powder was studied using scanning electron microscopy (SEM).

## MATERIALS AND METHODS

Cotton fiber as raw material was obtained from local market. The fiber was shredded and grinded for sufficient contact with chemical solution. The cellulose fibers were treated for five hours with various concentration of sodium hydroxide solution (5–50%). The excess sodium hydroxide from the pretreated fibers was removed by filter press. Monochloroacetic acid (MCA) with purity of 99.8% (Merck, Germany) was dissolved in distilled water with 30, 35, 40 and 45 weight % of MCA. The pretreated alkali cellulose was reacted with MCA. The mixture was stirred at 600 rpm on a magnetic hot-plate stirrer (VELP, Italy) at constant temperature of 75°C for four hours. Isopropanol (ISP) and water were used as solvents in this reaction. The CMC gel product was filtered from solvent. The pH was adjusted

to 7, the product was purified with methanol (Fluka, Germany), dried at 70°C in a conventional oven (Binder, Germany) for one hour [3, 5, 16, 17]. The solution pH was measured by pH meter, HANNA, model 21 (Italy).

The Na-CMC was easily dissolved in distilled water then extracted with 95% of ethanol (Fulka, Germany) as precipitated solid. The CMC product was removed from organic phase. The degree of substitution (DS) of CMC which is defined as a number of substituted sodium instead of –OH group on cellulose polymer has a maximum value of 3. The substitution of the hydroxyl groups by the carboxymethyl group perform preponderantly at C-2 of the glucose molecule [5, 18]. The DS of CMC was determined by standard method of ASTM D 1439 [19]. For less than 0.4 DS, CMC is swelled but insoluble in water; however, for DS of more than 0.4, CMC is fully soluble with its hydro-affinity, which increases with increasing DS [20]. The dried powder of CMC was analyzed with Fourier Transform Infrared (FTIR, Shimadzu Model 4100, Japan), to define the functional group of synthesized CMC. Scanning Electron Microscope (SEM) was used to take the image of the synthesized CMC samples. The samples were freeze dried (EMITECH; Model IK750, Cambridge, UK) on a polished aluminum surface. After drying, the sample was sputtered with gold for 30s by Polaron machine (BAL-TEC, Model SCDOOS, Switzerland). Afterwards, SEM was performed with a Stereoscan (Phillips XL30, Holland) Microscope.

## RESULTS AND DISCUSSION

The shredded uniform cotton fibers were pretreatment with sodium hydroxide solution. Active alkali cellulose was reacted with monochloroacetic acid solution. The primary treatment of pure cellulose fiber with variable weight percentage of NaOH in static solution and shredded fiber was conducted. The effect of sodium hydroxide solution on production of alkali cellulose is shown in Fig. 1. The amount of adsorbed NaOH for the shredded fiber was 39% higher than that in the static solution. The results revealed that the amount of adsorbed NaOH was proportional to concentration of NaOH solution. The concentration of NaOH in the production of alkali cellulose fibers was one of the influential parameter to explain the degree of substitution of MCA on cellulose fibers. The range of DS obtained

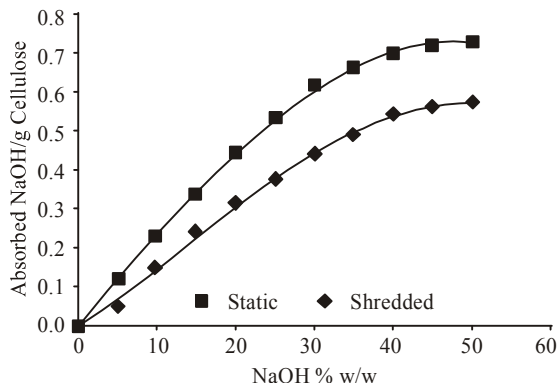


Fig. 1: Adsorption of NaOH on Alkali Cellulose by the shredded fibers and static solution

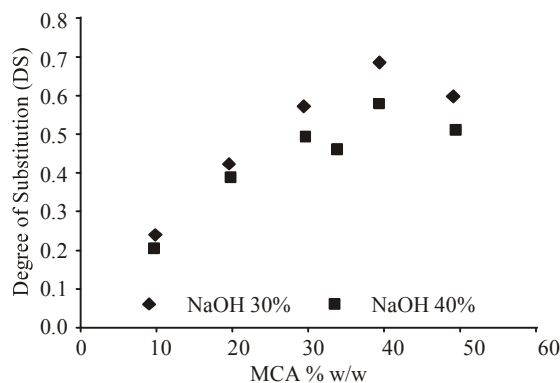


Fig. 3: Optimization of DS with respect to MCA concentration

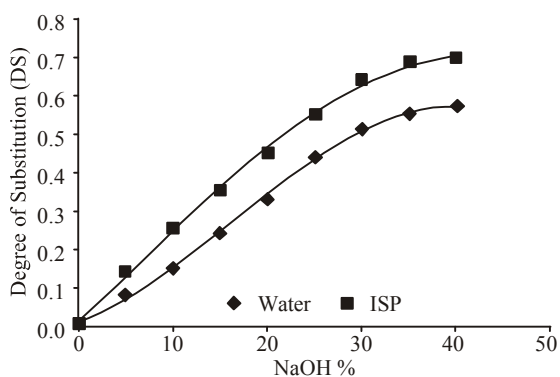
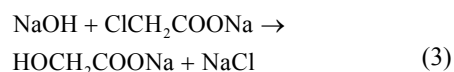


Fig. 2: Effect of sodium hydroxide concentration and solvent on degree of substitution in water and IPS

was from 0.15 to 0.7. Maximum amount of adsorbed NaOH with 50% of sodium hydroxide solution was 0.726 g per g of cellulose fibers.

Figure 2 demonstrates the effect of NaOH concentration on degree of substitution in presence of organic solvent and water. The use of isopropyl alcohol as solvent, the highest degree of substitution of NaOH on cellulose fibers, (DS of 0.7) was obtained. The role of organic solvent in the carboxymethyl cellulose reaction is to provide the accessibility of the reactants in the etherification of the cellulose chain. The polarity of organic solvent assisted the carboxymethylation of cellulose molecule. The polarity of isopropyl alcohol is less than that in water. As the polarity of the aqueous media decreased the efficiency of methylation reaction was increased [21]. The trend of results for the degree of substitution is depended on the NaOH concentration. Above 40% of NaOH, the degree of substitution was reached to a stable and fixed value.

Figure 3 depicts the DS of NaOH with respect to MCA for 30 and 40% of NaOH. The highest DS was obtained with 30% NaOH; however, additional NaOH may cause reduction in DS value. That was likely due to the sodium glycolate formation which is known as the byproduct in the synthesis of CMC [15, 17]. Polymer degradation was also occurred due to high concentration of NaOH [21, 2]. The reaction of MCA with additional NaOH is stated below:



The CMC samples were analyzed by FTIR [2, 23]. The spectrum is shown in Fig. 4. The x-axis represents Wavelength ( $\text{cm}^{-1}$ ) and y-axis shows the light transmittance through the sample. The FTIR spectrum of the sample shows that the carboxyl, methyl and hydroxyl functional groups are found at wavelength of 1618, 1426 and 1300  $\text{cm}^{-1}$ , respectively. According to reported data, the peaks at wavelength of 1620 and 1423  $\text{cm}^{-1}$  represented two different functional groups in CMC [2, 23]. The additional peaks at wavelength of 2152 and 2376  $\text{cm}^{-1}$  might be due to the existence of the contamination from impurities or combination band with water [2]. It is obvious that broad absorption band at 3432  $\text{cm}^{-1}$  is due to the stretching frequency of the hydroxyl group ( $-\text{OH}$ ). The band at 2909  $\text{cm}^{-1}$  is due to carbon-hydrogen bond ( $\text{C}-\text{H}$ ) stretching vibration. The presence of a strong absorption band at 1603  $\text{cm}^{-1}$  confirmed the presence of carboxyl group ( $-\text{COO}$ ). The bands around 1423 and 1325  $\text{cm}^{-1}$  are assigned to  $-\text{CH}_2$  scissoring and hydroxyl group ( $-\text{OH}$ ) bending

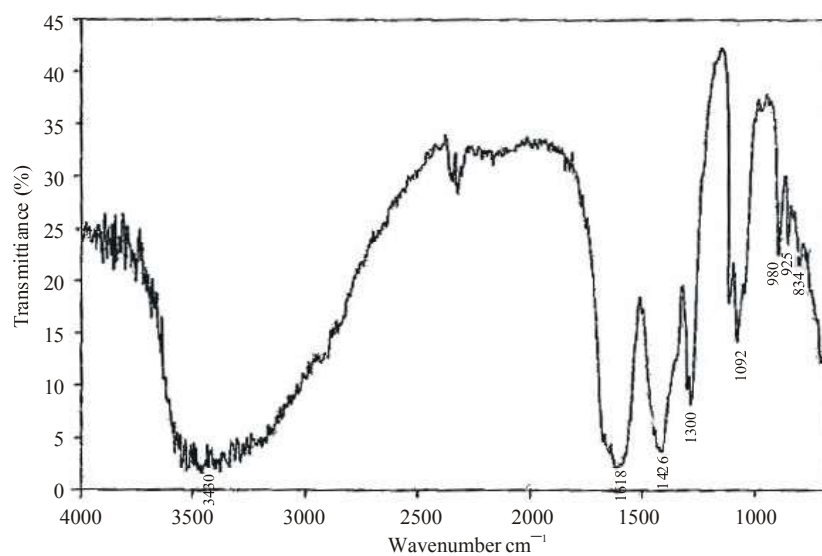


Fig. 4: FTIR spectrum of synthesized CMC sample

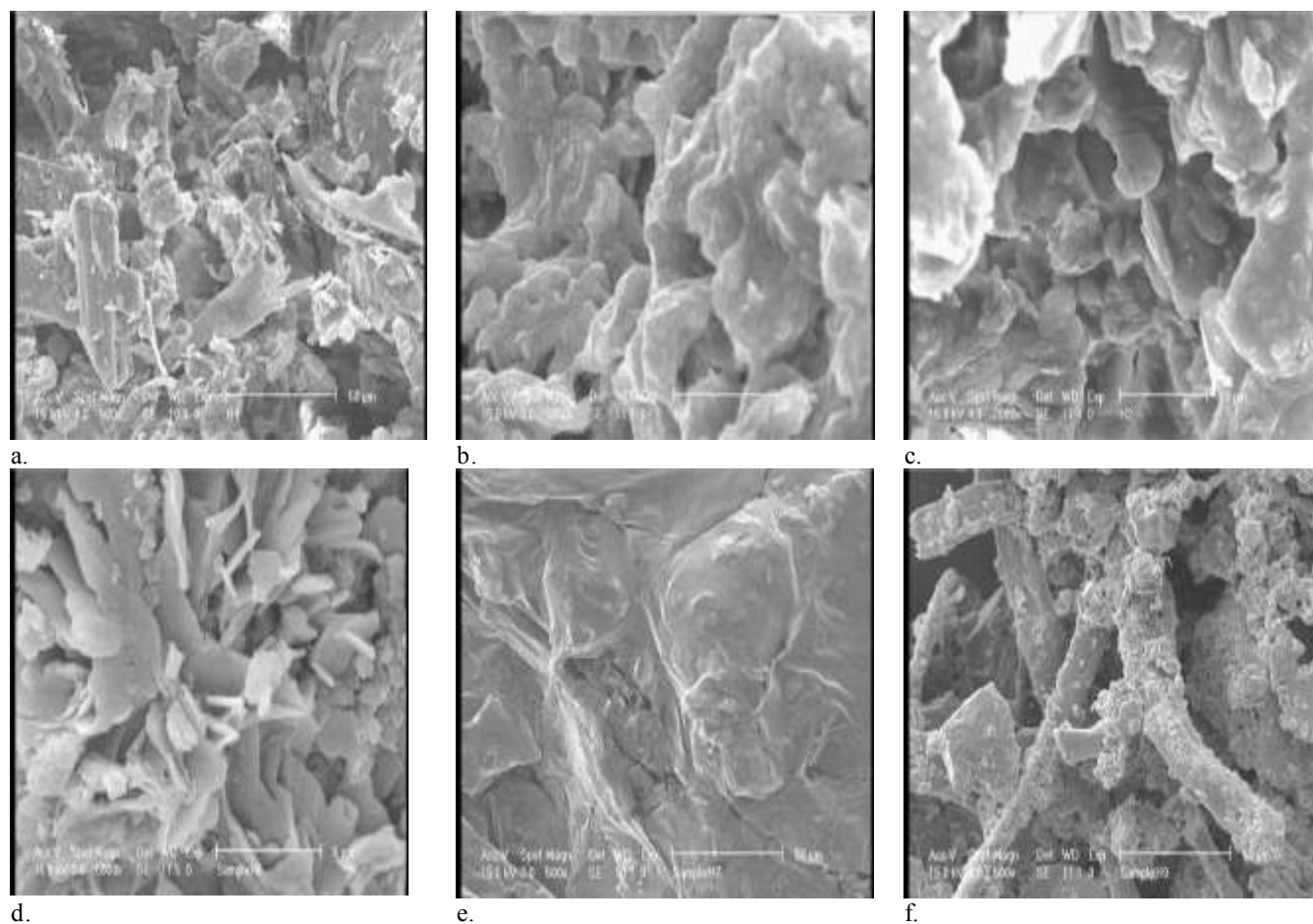


Fig. 5: SEM micrographs of CMC samples  
 a. 20%, b. 30% and c. 40% NaOH, the solvent used was water. d. 30% NaOH with ISP in basification  
 e. 30% NaOH with ISP in etherification f. Washed sample by methanol

vibration, respectively. The band at  $1061\text{ cm}^{-1}$  is due to  $>\text{CH}-\text{O}-\text{CH}_2$  stretching [24].

Figure 5 represents the SEM micrographs of various CMC powdered samples. The micrographs were prepared from the basified CMC samples with 20, 30 and 40% NaOH. The optimum NaOH solution for uniform product of CMC was 30 percent NaOH. The exterior surface of the CMC samples are shown that the cellulose fibers were methylated deeply. In the next stage of the reaction, etherification was carried out with MCA as the organic acid that was replaced by substitution of NaOH on cellulose fibers. The sample was washed and purified with methanol. The CMC products were prepared by several time alcohol wash up. Use of ISP as solvent was very effective in the preparation of the CMC as a desirable product with high DS (0.7). The glossy product was obtained in the etherification stage.

### CONCLUSION

CMC samples were successfully synthesized with alkali cellulose, in the presence of 30% NaOH under etherification with 40% MCA. The highest DS sample was obtained with ISP as solvent and the obtained CMC sample was glossy. Interestingly, the CMC powder was easily dissolvable in water.

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### REFERENCES

- Hattori, K., E. Abe, T. Yoshida and J. Cuculo, 2004. New solvents for Cellulose II ethylenediamine/thiocyanate salt system. *Polymer J.*, 36 (2): 123-130.
- Adinugraha, M.P. and D.W. Marseno, 2005. Haryadi, Synthesis and characterization of sodium carboxymethyl cellulose from cavendish banana pseudo stem (*Musa cavendishii* LAMBERT). *Carbohydrate Polymers*, 62: 164-169.
- Kirk, R.E. and D.F. Othmer, 1997. *Cellulose encyclopedia of chemical technology*, John Wiley, New York, 4: 593-683.
- Olaru, N., L. Olaru, A. Stoleriu and D. Timpu, 1998. Carboxymethyl cellulose synthesis in organic media containing ethanol and/or acetone. *J. Applied Polymer Sci.*, 67: 481-486.
- Togrul, H. and N. Arslan, 2003. Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. *Carbohydrate Polymers*, 54: 73-82.
- Xue, J. and M. Ngadi, 2009. Effects of methylcellulose, xanthan gum and carboxymethyl cellulose on thermal properties of batter systems formulated with different flour combinations. *Food Hydrocolloids*, 23: 286-295.
- Xiaojia, H., W. Shaozu, F. Dongkang and N. Jinren, 2009. Preparation of sodium carboxymethyl cellulose from paper sludge. *J. Chem. Technol. Biotechnol.*, 84 (3): 427-434.
- Dolz, M., J. Jiménez, M.J. Hernández, J. Delegido and A. Casanovas, 2007. Flow and thixotropy of non-contaminating oil drilling fluids formulated with bentonite and sodium carboxymethyl cellulose. *J. Petroleum Sci. Eng.*, 57: 294-302.
- Fijan, R., M. Basile, S.S. Turk, Z.M. Agar, M. Zigon and R. Lapasin, 2009. A study of rheological and molecular weight properties of recycled polysaccharides used as thickeners in textile printing. *Carbohydrate Polymers*, 76: 8-16.
- Mohanty, A.K., C.R. Simmons and M.C. Wiener, 2003. Inhibition of tobacco etch virus protease activity by detergents. *Protein Expression and Purification*, 27: 109-114.
- Jardebby, K., U. Germga, B. Kreutz, T. Heinze, U. Heinze and H. Lennholm, 2005. Effect of pulp composition on the characteristics of residuals in CMC made from such pulps. *Cellulose*, 12: 385-393.
- Varshney, V., P. Gupta and S. Naithani, 2006. Carboxymethylation of  $\alpha$ -cellulose isolated from *Lantana camara* with respect to degree of substitution and rheological behavior. *Carbohydrate Polymers* 63:40-45.
- Casey, J., 1981. *Pulp and paper: Chemistry and Chemical Technology*, John Wiley, New York, 3.
- Barba, C., D. Montane, M. Rinaudo and X. Farriol, 2002. Synthesis and characterization of carboxymethylcelluloses (CMC) from non-wood fibers I. Accessibility of cellulose fibers and CMC synthesis, *Cellulose*, 9: 319-326.
- Guo, Z., R. Xing, S. Liu, Z. Zhong and P. Li, 2008. Synthesis and hydroxyl radicals scavenging activity of quaternized carboxymethyl chitosan. *Carbohydrate Polymers*, 73: 173-177.

16. Lawal, O.S., M.D. Lechner and W.M. Kulicke, 2008. Single and multi-step carboxymethylation of water yam (*Dioscorea alata*) starch: Synthesis and characterization. *Intl. J. Biol. Macromolecules*, 42: 429-435.
17. deAbreu, F.R., P. Sergio and C. Filho, 2009. Characteristics and properties of carboxymethyl chitosan. *Carbohydrate Polymers*, 75: 214-221.
18. Charpentier, D., G. Mocanu, A. Carpov, S. Chapelle, L. Merle and G. Muller, 1997. New hydrophobically modified carboxymethyl cellulose derivatives. *Carbohydrate Polymer*, 33: 177-186.
19. ASTM (American Society for Testing and Materials), 2003. Standard Test Methods for Sodium Carboxymethylcellulose, ASTM D 1439-2003.
20. Waring, M. and J. Parsons, 2001. Physico-Chemical characterization of carboxymethylated spun cellulose fibres. *Biomaterials*, 22: 903-912.
21. Barai, B.K., R.S. Singhal and P.R. Kulkarni, 1997. Optimization of a process for preparing carboxymethyl cellulose from water hyacinth (*Eichornia crassipes*). *Carbohydrate Polymers*, 32: 229-231.
22. Mann, G., J. Kunze, F. Loth and H.P. Fink, 1998. Cellulose ethers with a block-like distribution of the substituent's by structure-selective derivatization of cellulose. *Polymer*, 39(14): 3155-3165.
23. Pecsok, R.L., L.D. Shields, T. Cairns and I.G. McWilliam, 1976. *Modern Method of Chemical Analysis*. John Wiley, New York.
24. Biswal, D.R. and R.P. Singh, 2004. Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers*, 57: 379-387.