Synthesis and Characterization of Carboxymethyl Cellulose using Solvents Variations

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Keywords: Carboxymethyl cellulose, degree of substitution, organic solvent.

Abstract: Carboxymethyl cellulose (CMC) is a cellulose derivative which is widely used in pharmaceutical and non-pharmaceutical industries. One of the important parameters in CMC synthesis is the variation of solvent medium. Solvents can affect the quality of CMC. The present study was conducted to synthesize and characterize of CMC with the best organic solvent mixture. CMC was obtained from microcrystalline cellulose by three stages, including alkalization between cellulose and sodium hydroxide with solvent; carboxymethylation using sodium monochloroacetate; neutralization and purification using glacial acetic acid-methanol. The solvent medium used were isopropanol-n butanol; benzene-ethanol-air; isopropanol-benzene; isopropanol-ethanol-air, and isopropanol-isobutanol by each variety of comparisons. CMC was characterized by Infrared Spectrophotometry. Degree of substitution and organoleptic test were then determined. The optimum condition of CMC synthesis which provided highest degree of substitution of 0.9 was found on isopropanol-ethanol solvents in ratio of 50:50. Organoleptic test showed that CMC powdered was colourless, rough, odorless and tasteless. Infrared analysis revealed the presence of carboxyl and ether functional groups in the 1600-1000 cm^{-1} region. It can be concluded that CMC has been succesfully synthesized using isopropanol-ethanol as the best solvent.

1 INTRODUCTION

One of cellulose derivatives that the most widely used is CMC. Many industries such as food, pharmaceutical, detergent, textile, cosmetic, and ceramic industries have used CMC as excipient (Koh, 2013). The study of Technavio London shows that the needs of CMC in the world will increase rapidly by 5% in 2017-2021 (Maida, 2017).

The increasing variety of CMC usage encourages the production of good quality CMC synthesis. CMC synthesis involves the conversion of cellulose into alkaline cellulose which then hydroxyl groups of cellulose are substituted by carboxymethyl groups by reacting them to sodium monchloracetate (Na-MCA) (Heinze and Pfeiiffer, 1999).

The process of CMC synthesis consists of several steps, namely alkalization, carboximethylation, purification, and neutralization. Alkalization and carboxymethylation reactions are steps that determine the value of the DS. The alkalization process aims to stretch the intramolecular and intermolecular hydrogen bonds of cellulose so easily substituted into carboxymethyl groups using NaOH in a suitable solvent. The number of substituted hydroxyl groups is called degree of substitution (DS) (Cash and Caputo, 2010). The solvent is used should be inert. It facilitates NaOH to penetrate well in reaction cellulose. The addition of NaOH is important in producing alkaline cellulose. The solvent also provides in sodium mono chloro acetic acid accessibility to AGU (anhydroglucose unit) cellulose reaction that occurs during CMC synthesis (Stigsson, 2006).

The quality of CMC can be obtained from several parameters. DS is the main parameter in determining quality of CMC, the DS value also states the solubility of CMC in water. The maximum degree of substitution for CMC is average value between 0.4 to 1.5. The higher degree of substitution of CMC, the easier solubility in water (Aambjornsson, 2015).

DS values are influenced by several factors, one of which is the type and composition of the solvent medium in alkalization step. The purpose of this research is conducted to synthesize and characterize of CMC with the best organic solvent mixture.

Yuliasmi, S., Wahyuni, H., Aisyah, H. and Riati, D.
Synthesis and Characterization of Carboxymethyl Cellulose using Solvents Variations.
DOI: 10.5220/0010093410151020
In *Proceedings of the International Conference of Science, Technology, Engineering, Environmental and Ramification Researches (ICOSTEERR 2018) - Research in Industry 4.0*, pages 1015-1020
ISBN: 978-989-758-449-7

2 METHODS

This research was conducted in two stages. First stage includes synthesis carboxymethyl cellulose using some solvents in different ratio. The second stage includes characterization of the syntesized carboxymethyl cellulose by Infra Red Spectrophotometry, degree of substitution, and organoleptic test.

2.1 Material

The materials used in the research were microcrystalline cellulose, distilled water, sodium hydroxide, sodium monochloroacetate (NaMCA), isobutyl alcohol, N-butanol, isopropyl alcohol, ethanol, methanol, benzene, glacial acetic acid.

2.2 Synthesis of Carboxymethyl Cellulose

This procedures followed the method of Safitri (2017) and Mulyatno (2017). 5 grams of cellulose was added to 100 ml of isopropyl alcohol, and 20 ml of NaOH while it was stirred in a temperature of 25°C for 1 hour. Then, added sodium chloroacetate to the mixture. The mixture was then heated while stirring at a temperature of 55ºC for 3 hours. Afterwards the mixture was filtered and the residue soaked using 100 ml of methanol for 24 hours. The mixture was neutralized using glacial acetic acid solution and then filtered. The residue was dried in an oven with a temperature of 60° C to a constant weight. The formula of CMC synthesis can be seen on Table 1.

Table 1: Design of formula synthesis of CMC.

Formula	Solvents	NaOH	NaMCA
	Isopropanol: N-Butanol	10%	4 grams
F1	80:20		
F2	50.50		
F3	30:70		
	Benzene:Ethanol:Water		
F4	70:20:10		
F5	50:30:20		
F6	50:50:0		
	Benzene:Isopropanol		
F7	30:70		
F8	50:50		
F9	70:30		
	Isopropanol:Isobutanol		
F10	70:30		
F11	50:50		
F12	30:70		
	Isopropanol:Ethanol: Water		
F13	70:20:10		
F14	50:50:0		

2.3 Characterization of Carboxymehyl Cellulose

2.3.1 The Organoleptic Properties Test

It included colour, taste, texture and odor.

2.3.2 Degree of Substitution Determination (DS)

Relative values of degree of substitution of carboxyl group in CMC could be analysed by IR spectra. By comparing absorbance of carboxyl group stretching vibration and methine stretching vibration (Rrel $=A_{1605}/A_{2920}$), we could evaluate the relative amount of carboxyl group in the sample. DSrel was calculated by the following equation (Singh and Khatri, 2012):

$$DSrel = Rrel_{(CMC)} - Rrel_{(cellulose)} \quad (1)$$

2.3.3 Infrared Spectrophotometry Analysis

All measurements were carried out using the KBr method. The samples were dried in an oven at 60◦C. Sample and KBr were mixed (1:100) then ground until homogenous. Afterwards the mixture was compressed to a form a transparent disk. The infrared spectra of these samples were recorded with a FT-IR Shimadzu Spectrophotometer between 400 and 4000 cm^{-1}.

3 RESULT AND DICUSSION

Synthesis of CMC was began by suspending the cellulose in a solvent using a mechanical stirrer at room temperature. The effect of solvent which is related to the ability of the reaction to dissolve the etherifying agents (NaMCA) and swell the cellulose to improve the accessibility NaMCA into cellulose structure. The right solvent ratio will increase the substitution of reaction, and if the ratio is not appropriate the reaction will be inhibited (Ismail, 2010).

The next process was carboxymethylation namely the addition of sodium monochloroacetic

($ClCH_2COONa$) with stirring for 3 hours at a temperature of 55ºC. Resulting by products such as sodium glycolate and sodium chloride at this stage. Separating CMC from the side product with added methanol and mixed. Neutralization of product was conducted because the reaction process running on alkaline conditions used acetic acid. CMC had been cleaned and then dried using an oven at a temperature of 60ºC (Musfiroh, 2013).

The influence of the type of solvent can be explained in terms of polarity and stereochemistry. Based on these properties, it is known that the smaller the value of the polarity of the solvent/reaction medium would increase the effectiveness carboxymethylation (etherification) and a smaller polarity solvent would also help keep the cellulose molecules were less decomposed by alkali. The formation of this layer makes the amount of NaOH were distributed in the cellulose phase enough to turn cellulose into cellulose-defined shapes (Stigsson, 2006) (Pitaloka, 2017).

In other words, the polarity of the smaller reaction medium would help the formation of alkali cellulose with a uniform distribution. This uniform distribution can be achieved because of low solubility in the alkaline solution non-polar system so that the hydroxyl group (OH) is not reactive with the Na+. Decreased reactivity of hydroxyl groups followed by a longer carbon chain (C) in alcohol. Larger methyl group can make the low reactivity of hydroxyl groups (Zhang, 1993). Polarity index of some organic solvent is showed on Table 2.

Table 2: Data polarity index from some solvent.

Solvent	Polarity Index
benzene	2.7
isopropanol	3.9
N-butanol	4
isobutanol	4
ethanol	5.2
water	9

3.1 The Organoleptic Properties

The results of the organoleptic synthesized CMC is show in Table 3. Table 3 shows that synthesized CMC has organoleptic with color is ivory, rough powder, odorless, and tasteless. Overall the synthesized CMC had similar organoleptic caracteritics except F6 until F9. From the table it can be seen that CMC produced using a solvent mixture of benzene has organoleptic with lump hard and colors are yellow to brown whereas the synthesized CMC using a solvent mixture of water has a white color and the form of a fine powder.

Table 3: The organoleptic properties of synthesized CMC.

Formula	Organoleptic			
	Colour	Texture	Odor	Taste
F1	Ivory	Rough powder	No	No
F2	Wheat	Rough powder	No	No
F3	Ivory	Rough powder	No	No
F4	White	Fine powder	No	No
F5	White	Fine powder	No	No
F6	Ivory	Lump hard	No	No
F7	Burlywood	Lump hard	No	No
F8	Ivory	Lump hard	No	No
F9	Burlywood	Lump hard	No	No
F10	Ivory	Rough powder	No	No
F11	Ivory	Rough powder	No	No
F12	Ivory	Rough powder	No	No
F13	White	Rough powder	No	No
F14	Ivory	Rough powder	No	No

3.2 Degree of Substitution Analysis (DS)

The maximum degree of substitution for CMC is 3 with an average value between 0.4 to 1.5. The higher degree of substitution of CMC, the more increase solubility in water (Aambjornsson, 2015). The results of DS analysis of CMC which have been synthesized are shown in Table 4.

As it is known, using a mixed of solvents in various composition ratio could affect the value of DS. From the table 4 below, it can be seen that CMC were synthesized using isopropanol solvent mixture has a higher DS compared to using a solvent mixture of benzene. It can be explained by the increasing composition of the solvent mixture of isopropanol, the rising of the polarity of a solution (Kalem and Johangir, 2007; Pitaloka, 2017).

Table 4: Degree of Substitution of CMC.

Formula	Solvents	DS
	Isopropanol: N-Butanol	
F1	80:20	0.523
F2	50.50	0.522
F3	30:70	0.561
	Benzene:Ethanol:Water	
F4	70:20:10	0.412
F5	50:30:20	0.382
F6	50:50:0	0.751
	Benzene:Isopropanol	
F7	30:70	0.694
F8	50:50	0.628
F9	70:30	0.623
	Isopropanol:Isobutanol	
F10	70:30	0.797
F11	50:50	0.890
F12	30:70	0.757
	Isopropanol:Ethanol: Water	
F13	70:20:10	0.887
F14	50:50:0	0.906

Microcrystalline cellulose was used as the main ingredient of CMC manufacture had polar properties, wherein the cellulose will be easier to expand with more polar solvents. In addition, the use of isopropanol during synthesis CMC was known to produce fewer side reactions such as sodium glycolate (Im, 2018).

Based on Table 2, the polarity index of water was higher than ethanol, but the value of DS decreased with increasing the ratio of water used in the solvent mixture. This is due to the small molecular weight of water, while the microcrystalline cellulose has a large molecular weight. So that cellulose can not mix with the water because of differences in molecular weight which quite large.

At high water content also maked the cellulose was more decomposed by alkali and could damage the destruction of the cellulose crystal structure, which inhibits the diffusion of small reagent molecules into it. It caused more NaOH and NaMCA were remained in the solvent. In addition, the CMC product thus obtained had fewer degree of substitution and could be easily decomposed by alkali. The solvent with high water content were more polar than low moisture content. These factors lead to more side reactions, thus decreasing the availability of NaMCA and the degree of substitution for CMC (Zhang, 1993). This applies also to the mixture of isopropanol mixed solvents or benzene mixed solvents having a lower DS value compared to a mixture of waterless solvents.

The synthesized CMC using a solvent mixture of isobutanol obtained a higher DS value than using a solvent mixture of n-butanol. Although the polarity index value of isobutanol and n-butanol is the same, but the solvent mixture is influenced by the composition of its chemical structure.

In this study, using a solvent with a mixture of benzene and isopropanol was obtained a higher DS value compared with a mixture of benzene and ethanol. This shows that the solvent mixture has a high polarity index difference will cause a decrease in the value of DS. According to Zhao (2003) benzene would adjust the polarity of the solvent system. The lower polarity was achieved by increased the percentage of benzene, which tends to decreased solvent accessibility and NaOH to the cellulose chain. The CMC structure showed the crystal structure of the CMC synthesized with benzene completely destroyed and the CMC chain is cleary expands by the solvent.

Of the various types and compositions of solvent were used in this study, the maximum DS value was obtained on Isopropanol: Ethanol solvents (50:50), by 0.9. Increased accessibility of solvents and etherification reactants into the cellulose can increase of the rate of reaction, thereby increasing the DS and viscosity of the CMC solution.

When the solvent contains high levels of alcohols, cellulose will be more easily alkalized. The alkalized cellulose possesses less crystalline aggregation. This causes the reaction to be faster and to result a higher DS value. The molecular weight of the product has a relationship to alcohol content as well as to the other caracteristics (Zhang, et, al, 1993).

On the other hand, the microcrystalline cellulose has a smaller particle size so it has a large surface area. This will affect cellulose swelling in the solvent, which will affect the quality of the CMC produced.

3.3 Analysis of FTIR

FTIR analysis is carried out by comparing the commercial microcrystalline cellulose and CMC which can be seen in Figure 1. From the figure can be seen the differences between the spectrum of microcrystalline cellulose and carboxymethyl cellulose. In the area of wave number 3000 – 2850 cm^{-1} and 1200-1000 cm^{-1}, a commercial CMC had a slighter spectra than microcrystalline cellulose.

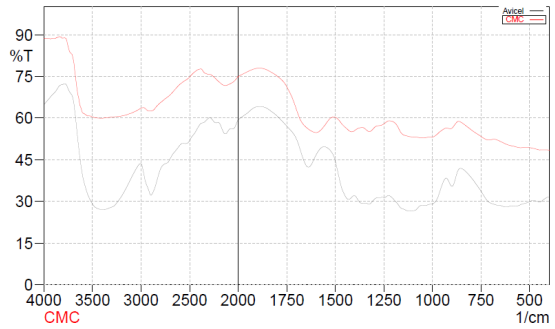

Figure 1: IR spectrum between CMC commercial and microcrystal cellulose.

In addition, FTIR analysis of synthesized CMC which had a maximum DS value with solvent Isopropanol: Ethanol (50:50) is shown in Figure 2. It indicated some point absorption at 1600.92 cm^{-1} and 1415.75 cm^{-1}. The highlights of the spectrum at a wave number of 1600.92 cm^{-1} with strong absorption indicates the presence of carbonyl group (COO), and at 1415.75 cm^{-1} indicates methyl ($-CH_2$). It demonstrated a carboxymethyl had been substituted in structure of the synthesized Na-CMC. Carboxyl group as salt structures had a range of waves ranging between 1600-1640 cm^{-1} to 1400 to 1450 cm^{-1}.

Furthermore, based on the analysis of FTIR of synthesized CMC were obtained the stretching vibration in some wave numbers, namely at 3421.72 cm^{-1} indicated the -OH group, 2893.22 cm^{-1} to 2927.94 cm^{-1} showed -CH aliphatic. Figure 2 illustrated the comparison of the infrared spectrum of commercial CMC and synthesized CMC. It showed similar spectrum and functional groups in both of them.

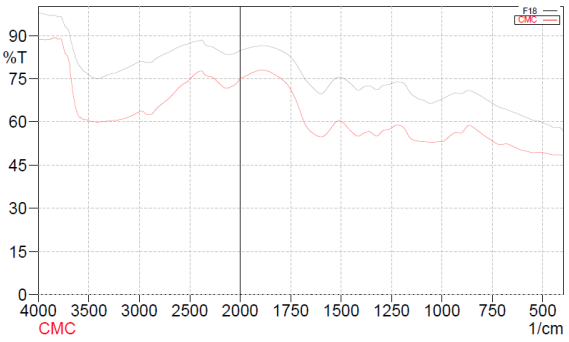

Figure 2: IR spectrum between commercial CMC and synthesized CMC by Isopropanol: Ethanol (50:50)

4 CONCLUSIONS

Quality of the synthesized CMC is affected by the solvent used. This study found that synthesis CMC using mixed solvents content of water and solvent with high polarity distinction would produce CMC with a low degree of substitution values. In this work, CMC was successfully synthesized using the best solvent consisting of a mixture of Isopropanol: Ethanol (50:50) with a DS value of 0.9 on the addition of 10% NaOH at 55°C for 3 hours, and 4 grams NaMCA.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge that the present research is supported by Universitas Sumatera Utara. The support is under the research grant TALENTA USU of Year 2018 Contract Number 2590/UN.5.1.R/PPM/2017 on 16th March 2018

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