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The Effect of Isopropyl Alcohol- 2-Butanol Mixed Solvent on Degree of Substitution of Carboxymethyl Cellulose from Water Hyacinth (*Eichhornia Crassipes*) Cellulose

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Abstract

Carboxymethyl cellulose (CMC) is one of the most important cellulose derivatives in various industrial uses. Non-wood cellulose resources have been utilized recently as raw material for production of CMC. Water hyacinth has rapid growth rate and contains relatively high cellulose content, which makes it potential of becoming non-wood cellulose source for the CMC synthesis process. In the present study, synthesis of CMC was conducted by using water hyacinth cellulose as raw material and employing mixtures of two solvent as a reaction medium, those are isopropyl alcohol and 2-butanol with NaOH concentration of 10%-weight. Influence of reaction medium composition on the degree of substitution (DS) was investigated. This mixed solvent which is used as reaction medium with various composition, that is 20:80, 50:50, and 80:20, will provide various polarities that affect the crystallinity of alkali cellulose. CMC production involves two steps, which are alkalization and carboxymethylation process using NaOH solution for 1 h at room temperature and sodium monochloroacetate as etherification substance conducted for 3.5 hours at 55^{o}C, respectively. The observed characteristics of CMC product include morphology, functional groups, and the DS. In this research, the maximum DS value of water hyacinth CMC was achieved at reaction medium composition of 50:50. This result is in agreement with crystallinity degree of alkali cellulose that was calculated from x-ray diffractogram.

Keywords: water hyacinth; cellulose; carboxymethyl cellulose; degree of substation; isopropyl alcohol-2-butanol mixture.

INTRODUCTION

Carboxymethyl cellulose (CMC) is one of cellulose derivatives, i.e. cellulose ether, with carboxymethyl groups (-CH_2-COONa) attached to hydroxyl groups in the cellulose main chain. CMC, that used renewable resources as raw material, is biodegradable and nontoxic. Recently, they have attracted much interest and met an increasing number of applications.

There are numerous grades of CMC. CMC with high purity, which has low salt content, has become a valuable additive in many fields. As an important cellulose derivative, CMC is widely used in food and pharmacy industries, detergent, and cosmetics [1]. For example, in instant noodle production, CMC is used as gluten to expand the wheat starch [2]. Carboxymethyl cellulose also used as preservative coating in fresh fruits, mud in oil drilling process, pigment thickener in textile industries, improving the quality of paper, and raw material of hydrogel synthesis [3-7].

Recently, non-wood cellulose resources, such as sugarcane bagasse, sugarcane straw, rice stubble, orange peel, grapefruit peel, corn husk, corncub, cornstalk, and seaweed have been utilized as raw material for production of CMC [8-16]. Water hyacinth (*Eichornia crassipes*), which is also non-wood cellulose resources, contains relatively higher cellulose content (72.63%) among all uncultivated non-wood plants. Hence, water hyacinth is a potential source of cellulose. In addition, relatively low lignin content (8.93%) makes it easier to remove lignin from water hyacinth in order to obtain high purity cellulose [17]. Water hyacinth is known as an aquatic weed that can be easily cultivated as it can rapidly grow to very high density over 60 kg/m^2 [18]. Moreover, water hyacinth which contains significantly high cellulose content is potential to be utilized as raw material for CMC production, while it is also readily available in great abundance.

The property of CMC highly affected by the value of degree of substitution (DS), which is the average sum of hydroxyl groups of cellulose that is substituted by carboxymethyl group with maximal value of 3 [19]. The researchers are developing various methods to attain higher DS value that it would result in better commercial products [20]. One of the factors affecting the DS value of CMC is the medium used in the synthesis process. The role of solvent used in this process is its ability to dissolve etherification substance, such as sodium monochloroacetic acid (NaMCA), and to swell cellulose thus made the etherification substance easier to enter the structure of cellulose [20].

Previous studies reported synthesis CMC using various reaction medium. For example, synthesis of CMC from cotton linters employing a mixture of benzene and ethanol as reaction medium [21], CMC from sago waste using reaction medium of water, dimethylformamide (DMF), methanol, dimethylsulfoxide (DMSO), isopropyl alcohol, ethanol, butanol, and mixture of water and isopropyl alcohol [22], and CMC from orange peel cellulose with isobutyl alcohol as reaction medium [11]. Numerous mixtures solvent employed as reaction medium in the synthesis process of CMC are also reported, such as a mixture of isopropyl alcohol and water [23], water and ethanol mixtures [24], ethanol and isopropyl alcohol mixture [25], also a mixture of dimethyl sulfoxide (DMSO) and tetrabutylammonium fluoride trihydrate (TBAF) [26].

Polarity and stereochemistry of organic solvents also affect the carboxymethylation process, the lower the polarity the more efficient the reaction thus resulting in higher DS value of the product [27]. Isopropyl alcohol solvent has already widely used as reaction medium in CMC synthesis process. Mixing 2-butanol with isopropyl alcohol is expected to result in lower polarity of reaction medium and then obtain higher DS value because 2-butanol has lower polarity than isopropyl alcohol [28].

Only a few researches about CMC synthesis from water hyacinth has been conducted. CMC synthesis from water hyacinth cellulose using isopropyl alcohol, isobutyl alcohol, ethanol and water as reaction medium was observed [27]. The highest DS value achieved is 0.72. The synthesis of CMC from water hyacinth cellulose by using various mixtures of alcohol solvent as reaction medium has previously been studied. For example, a mixture of ethanol and isobutyl alcohol [29], isopropyl alcohol and ethanol [30], as well as isopropyl alcohol and isobutyl alcohol [31]. In this research CMC synthesis from water hyacinth cellulose use mixture of isopropyl alcohol and 2-butanol as medium reaction. The morphology, functional group, degree of crystallinity (X), and DS value of CMC, will be observed.

MATERIALS AND METHODS

Materials: The material used in this research is water hyacinth stems from Tangerang, Indonesia. Analytical grade chemicals were used in the current study. Chemicals for cellulose isolation are sodium chlorite $NaClO_2$ which is obtained from Sigma Aldrich, whereas acetic acid glacial CH_3COOH and sodium hydroxide NaOH were obtained from Merck. Distilled water and ethanol were used for cleaning and purifying cellulose products. NaOH and sodium monochloroacetic NaMCA (Sigma Aldrich) are used for alkalization and carboxymethylation process in CMC synthesis. The mixture of isopropyl alcohol and 2-butanol as reaction medium in this process were obtained from Merck. The final product is neutralized and washed with acetic acid glacial and ethanol.

Isolation of Cellulose from Water Hyacinth

The cellulose isolation process was performed before CMC synthesis process. These both processes use the same method as previous researches [31]. Cellulose isolation process started by drying water hyacinth stem. Dried water hyacinth stem was ground and passed through a 60 mesh sieve. Afterwards, water hyacinth powder was extracted to remove wax content (dewaxing) using toluene-ethanol mixed solution with ratio 2:1 (v/v). Then, bleaching process was performed to remove lignin content lignin using acetic acid solution 0.05 N that contains 1%-weight sodium chlorite, $NaClO_2$, at 80^{o}C for 3 hours. Hemicellulose content removed from water hyacinth powder using sodium hydroxide NaOH 17.5%-weight for 3 hours at room temperature. Further, sample filtered, neutralized using acetic acid glacial and washed with distilled water and ethanol.

Carboxymethyl Cellulose (CMC) Synthesis

CMC synthesis process consists of two main step, those are alkalization and carboxymethylation. For alkalization process, 5 gr cellulose was added in 100 ml reaction medium. Then, 20 ml NaOH solution added and stirred for 1 hour at room temperature. After alkalization process completed, carboxymethylation process was performed by adding 6 gr $ClCH_2COONa$ (sodium monochloroacetate/ NaMCA) gradually with stirring. Carboxymethylation process occurred for 3.5 hours at 55^{o}C. CMC products were then neutralized with acetic acid glacial and washed using ethanol to remove residual byproduct. Afterwards, washed CMC products were dried. The CMC synthesis is conducted with 10%-wt of NaOH solution and the medium of reaction composition was varied. The ratio of isopropyl alcohol and 2-butanol mixture as reaction medium are 20:80, 50:50, and 80:20, in ml.

Characterization of CMC

CMC characterization includes morphology using scanning electron micrograph (SEM), functional group from Fourier-transform infrared (FTIR) spectra, degree of crystallinity from x-ray diffraction (XRD) spectra which is calculated using Zhang *et al*. (1993) method [32], and the degree of substitution (DS). DS value is analyzed with several procedures [29]. The CMC sample, in the amount of 0.5-0.7 gram weight in dry basis, is weighed and wrapped in filter paper. Then, it is ignited in crucible in high temperature. After that, the crucible is cooled and placed in a 500 ml beaker glass. The next step is added 250 ml of water and 35 ml of N/10 H_2SO_4 by a pipet then boiled for 30 minutes. The solution is titrated with N/10 KOH by using phenolphthalein as the indicator. The DS value can be determined by Eq. (1):

$$DS = \frac{(162)(A)}{1000 - (80)(A)} \quad (1)$$

$$A = \frac{af - bf_1}{\text{weight samples in dry basis}\,(g)} - *\text{alkalinity}\,(\text{or} + \text{acidity}) \quad (2)$$

Where:

a: The volume of N/10 H_2SO_4 used (ml)

b: The volume of N/10 KOH used(ml)

f : The factor of N/10 H_2SO_4

f_1: The factor of N/10 KOH

(*): Alkalinity or Acidity

As it concerns that if the value is (+), it is alkalinity. On the other hand, when the value is (-), it is acidity.

From Eq. (1) and (2), there is alkalinity or acidity that influence the value of DS. The alkalinity and acidity of the samples are measured by adding 5 ml of N/10 H_2SO_4 and the solution then boiled for 10 minutes. It is titrated with N/10 KOH using phenolphthalein as the indicator. A blank test without CMC to measure the alkalinity or acidity is held at same time and procedure. Using the following formula for calculation:

$$\text{Alkalinity}\,(\text{acidity}) = \frac{(B - S)(f_1)}{\text{Weight of samples in dry basis (g)}} \quad (3)$$

Where:

B: The volume of N/10 H_2SO_4 used for CMC (ml)

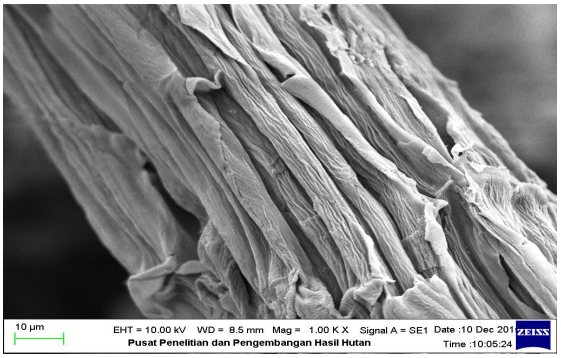
S: The volume of N/10 H_2SO_4 used for blank test (ml)

RESULTS AND DISCUSSION

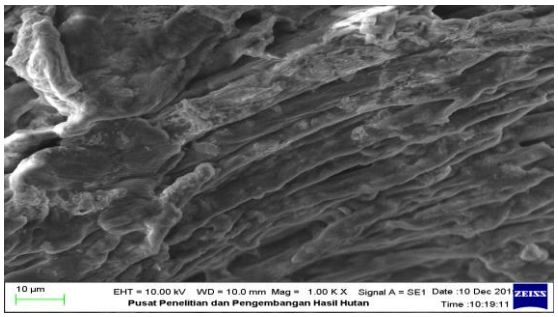
Morphology

The change of morphology from water hyacinth cellulose to alkali cellulose, then CMC by using 1000 times magnification is shown in figure 1. Surface morphology of cellulose fiber shows in figure 1a. Figure 1a illustrates that water hyacinth cellulose fibers are composed of a bundle of cellulose microfibrils as an imperfect array of elementary fibrils.

According to Habibi *et al.* (2010), approximately 36 molecules of cellulose are assembled together, generating elementary fibrils, and these are brought together, creating larger unit called microfibrils. A bunch of microfibrils produced cellulose fibers [33]. Its surface changes into irregular form after alkalization process as shown in figure 1b. This is as a result of the damaged of cellulose crystalline structure by NaOH and becomes amorphous phase. The alkalization process produces alkali cellulose (cellulose-O^- Na^+) [32]. By carboxymethylation process which produces CMC, the surface morphology is more irregular due to the substitution of carboxymethyl group on cellulose chain (figure 1c).



(a)



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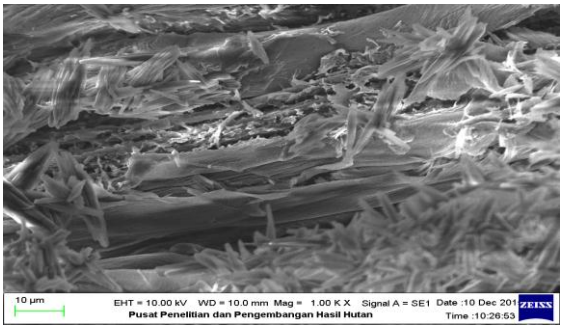

(c)

Figure 1: Scanning electron micrographs with 1000 times magnification (a) water hyacinth cellulose; (b) alkali cellulose (Na-Cellulose); (c) carboxymethyl cellulose (CMC)

Fourier-Transform Infrared Spectroscopy (FTIR)

In FTIR spectra, the formation of CMC is marked by the peak of carboxymethyl group, which are shown at 1640-1600 cm^{-1} and 1450-1400 cm^{-1} [34]. Figure 2 is the characteristics of CMC formation. FTIR spectra for CMC that is produced with mixture of isopropyl alcohol and 2-butanol as reaction medium show the peak at 1613 cm^{-1} and 1415 cm^{-1}. This FTIR spectra proves that the formation CMC.

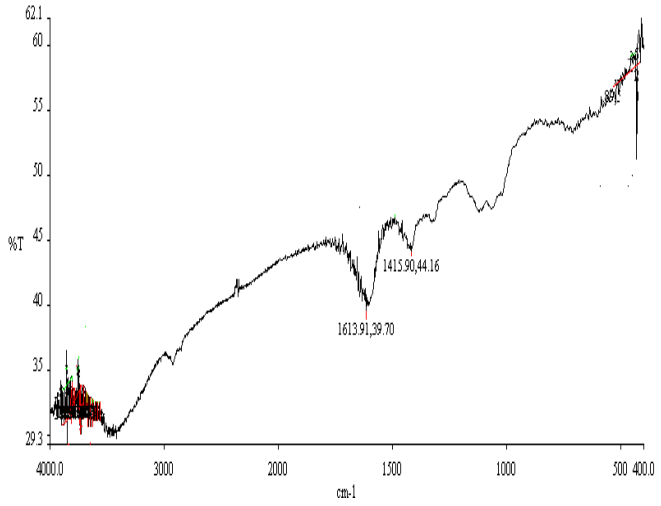

Figure 2: FTIR spectra of CMC with mixture of isopropyl alcohol and 2-butanol as reaction medium of 50:50 composition in NaOH 10%-wt

X-Ray Diffraction (XRD)

Crystallinity degree was evaluated using x-ray diffractogram to investigate the influence of alkalization process on crystallinity changes and the percentage of crystalline phase from alkali cellulose. Crystalline structure changes play a significant role in carboxymethylation reaction process that will determine degree of substitution value of produced CMC.

Figure 3 shows X-ray diffractogram of alkali cellulose. Cellulose alkalization process causes the change in crystal structure of cellulose. The initial form of cellulose crystalline, called by cellulose I or natural cellulose, are partially damaged by NaOH. Then, the cellulose I change into amorphous form and become alkali cellulose (cellulose-O^- Na^+). This amorphous form will orientate and combine into another crystalline form, called cellulose II. Generally, these three forms of cellulose exist in an equilibrium [32].

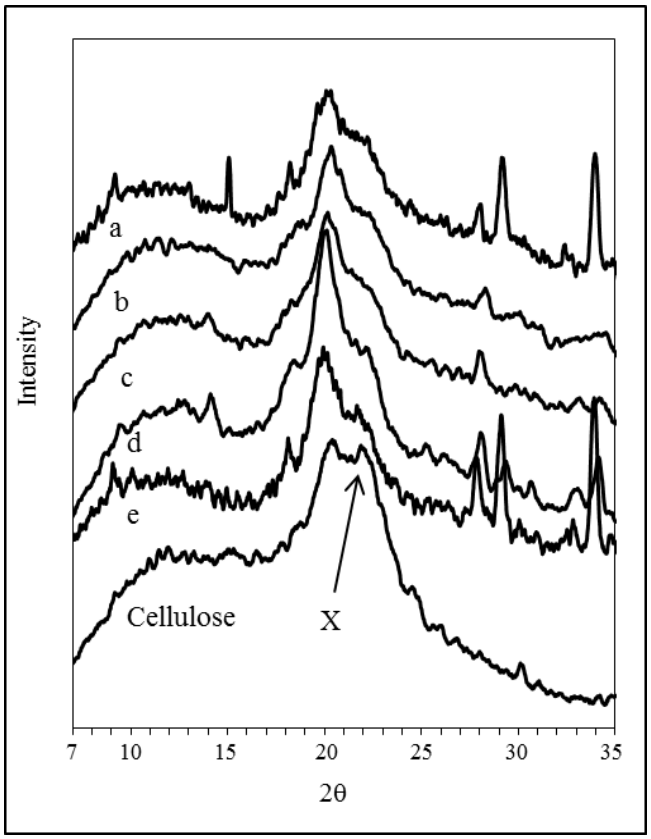

Figure 3: X-ray diffraction (XRD) of alkali cellulose on concentration of NaOH 10%-w using medium (a) pure isopropyl alcohol (b) 20%-v 2-butanol; (c) 50%-v 2-butanol; (d) 80%-v 2-butanol; (e) pure 2-butanol

According to Zhang *et al*. (1993), characteristic of cellulose I is marked with presence of peaks at angles (2θ): 9.0°; 14.7°; 16.1°; 22.4° and 34.2°, while for cellulose II at angles (2θ): 9.5°; 12.0°; 20.0°; 21.5° and 30°. The characteristics of cellulose I in water hyacinth cellulose is shown with the presence of peaks at angles around 15° and 22.5°. After

alkalization process with aqueous solution of NaOH 10%-wt, peak at around 22^o weaken (at Fig. 3 is shown with A) and disappeared, then to be followed by peak appearance at around 20^o or 21^o which is the characteristics of cellulose II [32]. From XRD spectra, it can be explained that cellulose of water hyacinth changes in crystalline phase from cellulose I to cellulose II after alkalization process. According to the statement of Zhang *et al.* (1993), cellulose II is formed from amorphous phase as a result of damaged cellulose I by solution of NaOH and these three phases exist in equilibrium. Therefore, the alkalization process of water hyacinth has a significant role in carboxymethylation process.

The changes in cellulose crystallinity may be due to partition of NaOH between reaction medium and cellulose chain. This partition occurs when cellulose suspends in the mixture of organic solvent, water, and NaOH. In this system, organic medium has a role on distributing NaOH with water uniformly in cellulose [35] and to form aqueous solution of NaOH, which contains small portion of organic solvent, in cellulose phase.

Type and composition of organic solvent used for reaction medium have a significant role in structure transformation of cellulose during the alkalization process [23]. Isopropyl alcohol has higher polarity than 2-butanol [28]. In the process using pure isopropyl alcohol, which tends to dissolve more NaOH than 2-butanol, NaOH concentration around cellulose is relatively low and cause fewer changes in crystalline structure cellulose. As a result, degree of crystallinity (X) of process using isopropyl alcohol is higher than 2-butanol (as shown in Table 1). Whereas 2-butanol with lower polarity dissolve less NaOH, therefore NaOH concentration around cellulose is relatively high. This condition will increase decrystallization process of cellulose and polymorphism change from cellulose I to cellulose II during the alkalization process [23].

The using of 2-butanol and isopropyl alcohol mixture in various composition ratio as reaction medium affects the crystalline structure. The changes of crystalline structure (including decrystallization and changes from cellulose I to cellulose II) will exist in condition between pure 2-butanol and pure isopropyl alcohol, as seen on the degree of crystallization results (Fig. 4).

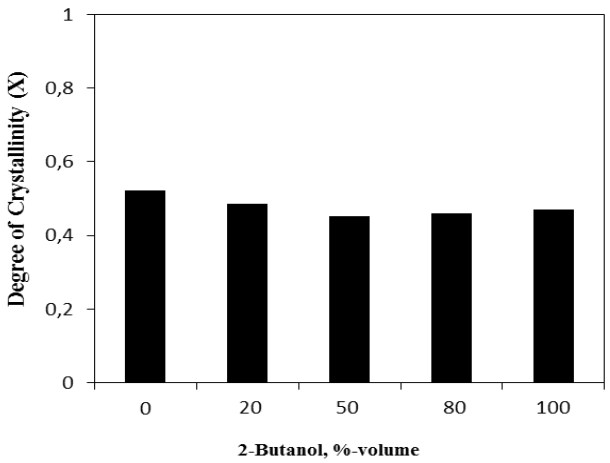

Figure 4: Degree of crystallinity (X) of alkali cellulose of 2-butanol and isopropyl alcohol mixture as a reaction medium

The composition of reaction medium 50:50 of 2-butanol and isopropyl alcohol, which corresponded to the lowest degree of crystallinity (Fig. 4), is an optimum condition for NaOH to damage the crystalline phase of natural cellulose into amorphous phase and produced alkali cellulose (cell-O$^-$Na$^+$) [32], hence it would be easier for reactant (NaMCA) to enter cellulose during carboxymethylation process. Furthermore, this composition provides exact NaOH concentration at phase of cellulose, therefore, higher amorphous phase and higher ratio of cellulose I to cellulose II can be obtained after alkalization process [23].

DEGREE OF SUBSTITUTION

It is inferred from fig. 5 that CMC produced using isopropyl-alcohol and 2-butanol as reaction medium results in higher DS value than using pure solvent. Transformation in cellulose structure could be the reason for the increase of DS value of CMC produced with this reaction medium. The maximum DS value of CMC is obtained at 50:50 of reaction medium composition at 2.07 (Fig. 5) that the lowest degree of crystallinity is achieved. The appropriate ratio of solvent mixture in reaction medium will enhance the substitution reaction of carboxymethyl group. On the other hand, if the ratio is not appropriate, it will become inhibitor of the reaction [20].This result is consistent with some research that shows the use of solvent mixture as reaction medium for alkalization and carboxymethylation process will produce higher DS value than using its pure solvent [1, 20, 23, 25].

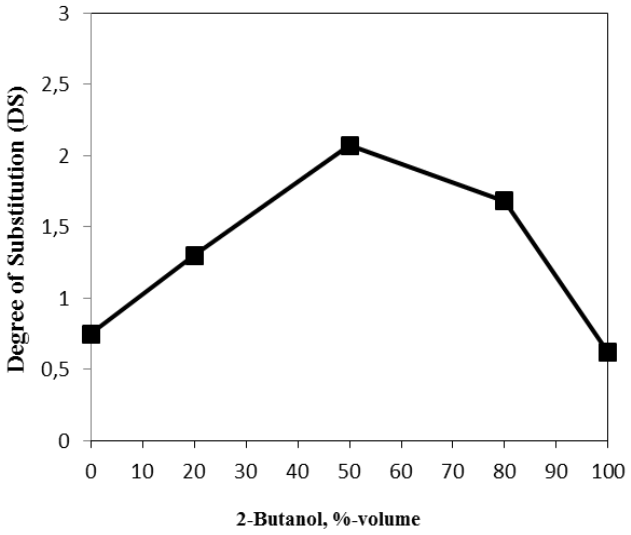

Figure 5: Effect of solvent ratio on DS of CMC with NaOH 10%-wt

CONCLUSION

The using of 2-butanol and isopropyl alcohol mixture as reaction medium on alkalization process result in better decrystallization of cellulose than its pure solvent. The highest DS value of CMC is obtained when the composition of reaction medium is 50:50, as well as the lowest degree of crystallinity, is achieved.

Table 1: Degree of Cristallinity of Alkali Cellulose with Pure Organic Solvent as Reaction Medium

Organic Solvent	Degree of Crystallinity
Isopropyl alcohol	0.523
2-Butanol	0.471

REFERENCES

[1] Olaru, N., Olaru, L., Stoleriu, A., and Timpu, D., 1998, "Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone", Journal of Applied Polymer Science, 67, pp. 481-486.

[2] Ahmad, M., 2013, "Sago's role as food stock in 21th century", International Journal on Advanced Science Engineering Information Technology, 3(4), pp. 15-17.

[3] Xue, J., and Ngadi, M,. 2009, "Effects of methylcellulose, xanthan gum and carboxymethyl cellulose on thermal properties of batter systems formulated with different flour combinations", Food Hydrocolloids, 23, pp. 286-295

[4] Dolz, M., Jiménez, J., Hernández, M.J., Delegido, J., and Casanovas, A., 2007, "Flow and thixotropy of non-contaminating oil drilling fluids formulated with bentonite and sodium carboxymethyl cellulose", Journal of Petroleum Science and Engineering, 57, pp. 294-302.

[5] Fijan, R., Basile, M., Turk, S.S., Zagar, E., Zigon, M., and Lapasin, R., 2009, "A study of rheological and molecular weight properties of recycled polysaccharides used as thickeners in textile printing", Carbohydrate Polymers, 76, pp. 8-16.

[6] Xiaojia, H., Shaozu, W., Dongkang, F., and Jinren, N., 2009, "Preparation of sodium carboxymethyl cellulose from paper sludge", Journal of Chemical Technology and Biotechnology, 84(3), pp. 427-434.

[7] Saputra, A.H., Hapsari, M., Pitaloka, A.B., and Wulan, P.P.D.K., 2015, "Synthesis and characterization of hydrogel from cellulose derivatives of water hyacinth (*Eichhornia crassipes*) through chemical cross-linking method by using citric acid", Journal of Engineering Science and Technology Special Issue on SOMCHE 2014 & RSCE 2014 Conference, pp. 75-86.

[8] Golbaghi, L., Khamforoush, M., and Hatami, T., 2017, "Carboxymethyl cellulose production from sugarcane bagasse with steam explosion pulping: Experimental, modeling, and optimization", Carbohydrate Polymers, 174, 780–788.

[9] Rodsamrana, P., and Sothornvit, R., 2017, "Rice stubble as a new biopolymer source to produce carboxymethylcellulose-blended films", Carbohydrate Polymers, pp. 94–101

[10] Yasar, F., Togrul, H., and Arslan, N., 2007, "Flow properties of cellulose and carboxymethyl cellulose from orange peel", Journal of Food Engineering, 81, pp. 187–199.

[11] Karatas¸ M., and Arslan, N., 2016, "Flow behaviours of cellulose and carboxymethylcellulose from grapefruit peel", Food Hydrocolloids, 58, pp. 235–245.

[12] Mondal, M.I.H., Yeasmin, M.S., and Rahman, M.S., 2015, "Preparation of food grade carboxymethyl cellulose from corn husk agrowaste", International

Journal of Biological Macromolecules, 79, pp. 144–150.

[13] Jia, F., Liu, H.J., Zhang, G.G., 2016, "Preparation of carboxymethyl cellulose from corncob", Procedia Environmental Sciences, 31, pp. 98 – 102.

[14] Shui, T., Feng, S., Chen, G., Li, A., Yuan, Z., Shui, H., Kuboki, T., Xu, C., 2017, "Synthesis of sodium carboxymethyl cellulose using bleached crude cellulose fractionated from cornstalk", Biomass and Bioenergy, 105, pp. 51-58.

[15] Lakshmi, D.S., Trivedi, N., Reddy, C.R.K., 2017, "Synthesis and characterization of seaweed cellulose derived carboxymethyl cellulose", Carbohydrate Polymers, 157, pp. 1604–1610.

[16] Joedibroto, R., 1983, "Prospek pemanfaatan eceng gondok dalam Industri Pulp dan Kertas/Prospect utilization of water hyacinth in the pulp and paper industry", Berita Selulosa, 19(1), pp. 33-37.

[17] Malik, A., 2007, "Review article Environmental challenge vis a vis opportunity: The case of water hyacinth", Environment International, 33, pp. 122–138.

[18] Kalia, S., Kaith, B.S., and Kaur, I., 2011, Cellulose Fibers: Bio- and Nano-Polymer Composites Green Chemistry and Technology, Springer – Verlag, Heidelberg, p. 47.

[19] Ismail, N.M., Bono, A., Valintinus, A.C.R., Nilus, S., and Chng, L.M., 2010, "Optimization of reaction conditions for preparing carboxymethyl cellulose", Journal of Applied Sciences, 10(21), pp. 2530-2536.

[20] Zhao, H., Cheng, F., Li, G., and Zhang, J., 2003, "Optimization of a process for carboxymethyl cellulose (CMC) preparation in mixed solvents", International Journal of Polymeric Materials, 52, pp. 749–759.

[21] Pushpamalar, V., Langford, S.J., Ahmad, M., and Lim, Y.Y., 2006, "Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste", Carbohydrate Polymers, 64, pp. 312–318.

[22] Olaru, N., and Olaru, L., 2001, "Influence of organic diluents on cellulose carboxymethylation", Macromolecular Chemistry and Physics, 202, pp. 207–211.

[23] Ruzene, D.S., Gonçalves, A.R., Teixeira, J.A., Amorim, M.T.P.D., 2007, "Carboxymethylcellulose Obtained by Ethanol/Water Organosolv Process Under Acid Conditions", Applied Biochemistry and Biotechnology, 136–140, pp. 573-582.

[24] Ruzene, D.S., Gonçalves, A.R., Teixeira, J.A., Amorim, M.T.P.D., 2007, "Carboxymethylcellulose Obtained by Ethanol/Water Organosolv Process Under Acid Conditions", Applied Biochemistry and Biotechnology, 136–140, pp. 573-582.

[25] Stigsson, V., Kloow, G., and Germgard, U., 2006, "The influence of the solvent system used during manufacturing of CMC", Cellulose, 13, pp. 705 – 712.

[26] Ramos, L.A., Frollini, E., Heinze, T., 2005, "Carboxymethylation of cellulose in the new solvent dimethylsulfoxide/tetrabutylammonium fluoride", Carbohydrate Polymers, 60, pp. 259–267.

[27] Barai, B.K., Singhal, R.S., and Kulkarni, P.R., 1997, "Optimization of a process for preparing carboxymethyl cellulose from water hyacinth *(Eichornia crassipes)*", Carbohydrate Polymer, 32, pp. 229-231.

[28] Reichardt, C., 2003, Solvents and Solvent Effects in Organic Chemistry, Third Edition, Wiley-VCH Verlag GmbH & Co. KGaA, p. 472.

[29] Saputra, A.H., Qadhayna, L., and Pitaloka, A.B., 2014, "Synthesis and characterization of carboxymethyl cellulose (CMC) from water hyacinth using ethanol-isobutyl alcohol mixture as solvents", International Journal of Chemical Engineering and Applications, 5, pp. 36-40.

[30] Pitaloka, A.B., Wijaya, S.M., Saputra, A.H., and Nasikin, M., 2014, "The effect of isopropanol-ethanol as reaction medium on degree of substitution of carboxymethyl cellulose (CMC) from water hyacinth (*eichhornia crassipes*) cellulose", Proceedings of The 27th Symposium of Malaysian Chemical Engineers (SOMChE 2014) in conjunction with 21st Regional Symposium on Chemical Engineering (RSCE 2014), PSE132, Taylor's University Lakeside Campus, Subang Jaya, Malaysia.

[31] Saputra, A.H., Hapsari, M., and Pitaloka, A.B., 2015, "Synthesis and characterization of CMC from water hyacinth using isobutyl-isopropyl alcohol mixture as reaction medium", Contemporary Engineering Science, 8, pp. 1571-1582.

[32] Zhang, J., Li, D., Zhang, X., and Shi, Y., 1993, "Solvent effect on carboxymethylation of cellulose", Journal of Applied Polymer Science, 49, pp. 741-

746.

[33] Habibi, Y., Lucia, L.A., and Rojas, O.J., 2010, "Cellulose nanocrystals: Chemistry, self-assembly, and applications", Chemical Reviews, 110(6), pp. 3479–3500.

[34] Adinugraha, M.P., Marseno, D.W., and Haryadi, 2005, "Synthesis and characterization of sodium carboxymethyl cellulose from cavendish banana pseudo stem *(Musa cavendishii LAMBERT)*", Carbohydrate Polymers, 62, pp. 164–169.

[35] Yokota, H., 1985, "The mechanism of cellulose alkalization in the isopropyl alcohol-water-sodium hydroxide-cellulose system", Journal of Applied Polymer Science, 30, pp. 263-277.