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Synthesis of carboxymethyl cellulose (CMC) from delignified *Dyera Costulata*

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Abstract

Carboxymethyl cellulose (CMC) was synthesised using Jelutong *(Dyera costulata*) plantation thinning biomass of 12 years old. The samples were delignified via pulping and bleaching process to remove lignin and hemicelluloses. The pulping process was carried out using 10% sodium hydroxide at various reaction times (1 – 5 hr) and temperatures (27 °C and 100 °C). The synthesis of CMC was carried out via alkalisation and etherification methods using sodium monochloroacetate. The sodium hydroxide concentration used during alkalisation varied from 30 to 50%. The highest yield of CMC obtained was 165%. The characterisation of CMC obtained includes its morphology structure, degree of substitution (DS), and reaction efficiency (RE). A higher DS value was obtained (0.723) for treated biomass (100 °C) with a higher concentration of sodium hydroxide used (40%) during synthesis. The CMC DS value obtained from this experiment falls within the commercial CMC DS values reported.

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1.0 Introduction

Lignocellulosic biomass containing cellulose is the most abundant resource available. Cellulose is a complex structure of polysaccharides with a high degree of crystallinity that was obtained via chemical, physical and biological breakdown (Pinto et al., 2022). Cellulose is linked by two main components which were hemicellulose and lignin and has an amorphous structure (Jung et al., 2015; Kucharska et al., 2018; Pinto et al., 2022). Alteration of physical and chemical properties of cellulose is reported to be able to augment its accessibility towards converting it into value-added products. Biomass for value-added products would facilitate to defeat of our economic issues by providing greener approach industries (Pushpamalar et al., 2006).

Jelutong (*Dyera costulata*) is a fast-growing and high-quality species available in Peninsular Malaysia within lowlands of secondary forests (Jeyanny et al., 2010). The fine exterior of the wood structure is appropriate for manufacturing furniture and wood-based products such as pencils, matches, and picture frames. Like other forestry species, Jelutong cellulose content is 40% as compared to hardwood which is 45 – 55% (Betts et al., 1991). Physically, cellulose is non-soluble in water. Conversion of cellulose into derivatives like carboxymethyl cellulose (CMC) turns it into the most important soluble derivative that is biodegradable, highly viscous, and harmless (Mat Soom et al., 2006; Huang et al. 2017; Ab Rasid et al., 2021). Its solubility is dependent on the degree of substitution (DS). DS is well-defined as the amount of substituted hydroxyl group per anhydrous glucose where the maximum DS is 3.0. Higher DS of CMC shows higher resistance to degradation which improves its compatibility with other soluble components (Ab Rasid et al., 2021). For the commercial grade of CMC, the DS value is within the range of 0.4 to 1.5 (Ambjörnsson, 2013; Rahman et al., 2020) and 0.2 to 1.2 (Bono et al., 2009).

Conversion of cellulose of lignocellulosic biomass into CMC would certainly increase the value of natural cellulose because its derivatives are extensively used in a wide range of industrial applications either for food or non-food industries since it is an environmental-friendly product (Ahemen et al., 2013; Tasaso, 2015; Parid et al., 2018; Tuan Mohamood et al., 2021). The most extensive use of CMC is in the production of paper, detergent, and paint. For pharmaceutical, food,

and personal care products, high grade and purity (>99%) of CMC is applied. Commercial CMC started to produce in the 1920s and today, the interest in CMC production has increased to fulfill the green chemicals and the biorefinery demand (Ulf & Alexander, 2006).

CMC production involved two-stage reactions that are alkalisation and etherification process using delignified biomass to form carboxymethyl groups that are very simple, low-cost, and efficient (Rachtanapun et al., 2012; Mohamad Zainol et al., 2021; Ab Rasid et al., 2021; Pinto et al. 2022). Delignification of biomass was carried out to remove lignin and hemicellulose to obtain high cellulose content (>95%). In the alkalisation stage, delignified biomass is treated using sodium hydroxide (15–50%) suspended in alcohol (organic) solvent normally isopropanol under stirring conditions (Pinto et al. 2022).

Alkalisation is an important process to ensure the alkali cellulose produced is highly reactive to react with sodium monochloroacetate in the etherification stage. Alkali cellulose is reacted with sodium monochloroacetate to produce carboxymethyl cellulose (CMC) with sodium glycolate and sodium chloride as by-products (Ambjörnsson, 2013; Mohamad Zainol et al., 2021; Ab Rasid et al., 2021).

Common types of solvent mediums used are isopropanol, ethanol, and methanol. The best solvent medium for alkalisation is isopropanol; a DS value of 0.558 was obtained for CMC produced from sago waste compared to other solvents tested (Pushpamalar et al., 2006). Hutomo et al. (2012) reported that the DS value of CMC synthesis from cocoa pod husk using isopropanol as solvent was 0.75. While the DS value of CMC produced from sugarcane bagasse was 0.78 (Asl et al. 2017).

In the commercial production of CMC, ethanol or isopropanol is mostly used as a solvent. Water cannot be used as a solvent as CMC is a water-soluble material and high consumption of monochloroacetic acid is required to recover the CMC (Ulf & Alexander 2006). The solubility of CMC in water has a strong relationship with the DS value, where increasing of DS value will increase its solubility in water.

This paper reports the production and characterisation of CMC from Jelutong plantation thinning biomass. The aim of this research is to add value to the Jelutong biomass generated during thinning exercise by synthesizing CMC. CMC is a prospective feedstock for various types of industries such as food, pharmaceutical, textiles, and paint industries. In future work, this CMC has the potential to be used as a carbon source for enzyme production from microbes either from fungi or bacteria.

2.0 Methodology

2.1 Raw materials

The 12 years old Jelutong biomass obtained from thinning of planted materials in FRIM was chipped, ground, and sieved to obtain particles of sizes less than 200 μm. The samples were then dried in the oven at 60 °C for 24 hr to constant weight with moisture content less than 10%.

2.2 Delignification of Jelutong biomass

About 10 g of samples were mixed with 100 ml of 10% sodium hydroxide (NaOH) solution. The mixture was stirred for 2 hr at room temperature. The pulped sample was filtered and washed using 95% ethanol and distilled water twice until a neutral pH was obtained (pH 7). The hemicellulose-free sample was then dried in the oven at 60 °C for 24 hr. The experimental work was carried out at two different reaction temperatures (i.e room temperature; 27 °C and 100 °C.) Then, the samples were bleached by adding 10 g of the pulped sample into 1 L conical flask and suspended in 500 ml hot distilled water together with 75 ml glacial acetic acid. 10 g of technical-grade sodium chlorite was added and the mixture was stirred for 3 hr at 70 °C. Then, the mixture was filtered and washed again with 95% ethanol and distilled water twice until a neutral pH was obtained. Finally, the residue was dried in the oven at 60 °C for 24 hr. This experiment was repeated for different pulped samples.

2.3 Synthesis of carboxymethyl cellulose (CMC)

2 g of delignified sample was mixed with 100 ml of 2-propanol and stirred for 1 hr at room temperature. Concurrently, 10 ml of 30% NaOH was added dropwise simultaneously with 3 g of sodium monochloroacetate into the mixture with continued stirring for another 30 minutes. The temperature was increased to 55 °C for another 3 hr with further stirring. The mixture was then filtered and soaked in 100 ml methanol overnight followed by neutralization using 10 ml alcoholic acetic acid in methanol (5% v/v). The solid sample was washed using 95% ethanol and dried in the oven at 60 °C degrees for 24 hr. The experimental work was repeated for a reaction time

range from 1 to 5 hr and different concentrations of sodium hydroxide (30–50%). The procedure used in the synthesis of CMC for the reaction temperature (55 °C) and type of solvent (isopropanol) during alkalisation was slightly modified from Palle (2008) and Pushpamalar (2006), respectively.

2.4 Surface morphology analysis of carboxymethyl cellulose (CMC)

Surface morphology analysis of the CMC was carried out using Scanning Electron Microscopy (SEM) FEI Quanta 200. CMC sample in powder form (particle size of 100 µm) was deposited and attached on specimen stubs. The surface morphology structures of Jelutong biomass raw, delignified, and CMC with a magnification of 1000× were obtained for comparison purposes. Morphology analysis was carried out to study the effect of each material obtained from each step based on its shape, size, and morphology structure.

2.5 Determination of chemical composition of raw and delignified Jelutong biomass

The chemical compositions of raw and delignified jelutong biomass were determined by carrying out analysis using TAPPI method on dry fibers. For alpha-cellulose (αC), lignin and extractives, it was determined by using TAPPI 203 om-93, TAPPI T236 om-13, and TAPPI T204 cm-17, respectively. While for holocellulose (Ho), the in-house method was used based on Wise et al. (1946), and hemicellulose (He) was calculated based on Eq. (1).

$$\text{Hemicellulose (\%)} = \text{Ho (\%)} - \alpha\text{C (\%)} \quad (1)$$

2.6 Characterisation of carboxymethyl cellulose (CMC)

The CMC produced was characterised by its product yield, degree of substitution (DS), reaction efficiency (RE), solubility, and pH. DS values were determined by adding 0.5 g of sample into 20 ml of 95% ethanol and stirring for 5 minutes. Subsequently, 10 ml of acetic acid was added to the mixture, boiled, and stirred for another 10 mins. The mixture was then filtered and washed using 75 ml of 80% ethanol. The residue was dried in the oven at 40 °C for 24 hr. About 0.2 g of dried CMC was weighed and mixed with 100 ml of distilled water and 25 ml of 0.3 M NaOH followed by boiling for another 20 minutes. One (1) drop of phenolphthalein indicator was added to the heated mixture. Then the mixture was titrated using 0.3 M HCl and the volume used was recorded. The DS value was calculated using Eq. (2) (Palle, 2008).

$$\text{Degree of substitution, } DS = 0.162\,A/(1 - 0.058A) \quad (2)$$

where, A=milli-equivalents of consumed acid per gram of specimen, ((BC – DE)/ F), B=volume of sodium hydroxide, C=concentration in normality of sodium hydroxide added, D=volume of consumed hydrochloric acid, E=concentration in normality of hydrochloric acid used and F=specimen grams used.

Reaction efficiency (RE) is one of the parameters used to optimise the CMC production reaction conditions. According to Palle (2008), RE measures the effectiveness of sodium monochloroacetate to substitute the hydroxyl groups in cellulose with carboxymethyl group. The percentage of RE for CMC produced was calculated using Eq. (3) (Palle, 2008);

$$\%\ RE = (W2 - W1)/\ W3 \times 100 \quad (3)$$

where, W1=weights of initial Jelutong raw (g), W2=weight of Jelutong CMC (g) & W3=weight of sodium monochloroacetate used (g)

3.0 Results and discussion

3.1 Chemical composition of Jelutong before and after delignification process

Preliminary studies were carried out on the properties of the raw and delignified Jelutong used to produce CMC. Delignification of Jelutong biomass affected the final content of alpha-cellulose, hemicellulose, lignin, and extractives content as shown in Table 1. The chemical composition after delignification depends on the parameter conditions during pulping and bleaching process. The chemical compositions of samples were analysed using TAPPI methods.

About 57.57% of alpha-cellulose was recovered after treatment at 100 °C using 10% sodium hydroxide. Delignification of Jelutong must be improved to recover more cellulose by increasing the pulping temperature and sodium hydroxide concentration. High-quality bleached pulp samples should have more than 95% of cellulose content to produce high-quality CMC based on its DS value (Mat Soom et al., 2006).

Table 1: Chemical composition of Jelutong before and after delignification

Composition	Before delignification	After delignification	Wood*
Holocellulose (%)	77.69	81.23	
Alpha-cellulose (%)	39.73	57.57	45-55
Hemicellulose (%)	37.96	23.66	24-40
Lignin (%)	30.47	18.91	18-25
Extractives (%)	5.28	2.16	

*Betts et al., 1991

Moreover, DS value of CMC very dependent on the holocellulose particle size where DS value will increase gradually with the decreasing size of holocellulose and particle size of 100 µm has produced CMC with DS value of 1.83 (Parid et al. 2018).

CMC was produced by comparing the DS value between raw and delignified Jelutong. The DS of CMC from delignified Jelutong (0.632) was higher than raw Jelutong (0.237), showing a relationship between DS value and the percentage of cellulose. Higher cellulose content gave a higher DS value of CMC. According to Palle (2008), lower alpha-cellulose content implies the existence of an excessive amount of low molar mass oligosaccharide (in hemicellulose) which affected the yield and quality of the CMC produced. High lignin and extractives content also gave an effect on the etherification process and reaction products.

3.2 Effect of reaction time during delignification of Jelutong biomass

Delignification of raw Jelutong involved two processes which are pulping and bleaching. In this study, the reaction times during delignification (pulping) of Jelutong biomass varied from 1 to 5 hr. The reaction times influenced the DS value and yield of CMC produced as shown in Fig. 1 with average standard deviation (SD) for DS and RE were 0.05 and 2.47, respectively. Initially, the DS value of CMC increased but after two (2) hours it started to decrease. This is due to the degradation of the polymer at prolonged reaction time (Palle, 2008). The highest DS value (0.632) was obtained for samples delignified for 2 hr. Here, the comparisons of DS values were made based on the synthesis of CMC that was carried out using a constant concentration of sodium hydroxide (30%) to study the effect of reaction times.

Furthermore, CMC produced can swell easily and has better contact with cellulose during the etherification process due to the application of sodium hydroxide as a catalyst to activate the carboxymethylation reaction. This result is similar to the CMC produced from Kenaf core using the same reaction conditions which gave a DS value of 0.69 (Palle, 2008) and 0.78 (Asl et al., 2017). According to Sophonputtanaphoca et al. (2019), the DS value affected by the NaOH concentration during the alkalisation where the DS value of CMC produced from rice straw varied from 0.63 to 0.87.

For reaction efficiency (RE), it shows the same pattern where RE values increased with the increasing of DS values. At higher DS value of about 0.632, the RE value obtained was 46.70%. The RE indicates the effectiveness of the sodium monochloroacetate reacted with hydroxyl groups of cellulose (Palle, 2008).

3.3 Effect of reaction temperature during delignification of Jelutong biomass

Reaction temperature is also an important parameter during delignification (pulping) of Jelutong biomass. More lignin and hemicellulose were removed by increasing the reaction temperature to 100 °C. The effect of reaction for both temperatures in Table 2 shows the comparison of CMC produced at different delignification reaction temperature during pulping process. It was found that, the increasing in temperature during pulping process has increased the DS value from 0.632 to 0.646. This is due to the modification of the chemical structure of the samples where more hydroxyl groups of cellulose have been replaced with carboxymethyl groups.

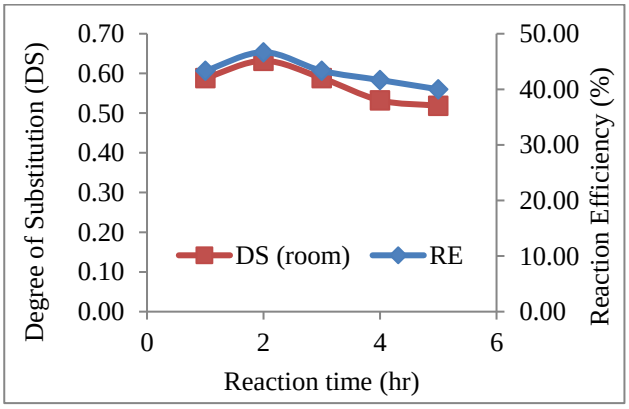


Fig. 1: Effect of reaction time during delignification of Jelutong on DS and RE value

Table 2: Comparison of CMC produced at different delignification reaction temperatures

Properties	CMC (Room temperature)	CMC (Temperature = 100°C
Degree of Substitution	0.6317	0.6463
pH	7	7
Product yield	1.70	1.75
Solubility	Both samples swell and soluble in water	

According to Ab Rasid et al. (2021), higher temperatures will increase the DS value due to the high swelling ability that could enhance the absorption and diffusion ability of sodium monochloroacetate into cellulose fiber at a higher temperature

3.4 Effect of sodium hydroxide concentration during synthesis of carboxymethyl cellulose (CMC)

Synthesis of CMC via the etherification process occurs in a controlled condition. Many factors influenced the yield of CMC such as reaction time, reaction temperature, and sodium hydroxide concentration. During the synthesis process, the bleached samples were pretreated using sodium hydroxide (known as alkalisation) to form active alkali cellulose. This active alkali cellulose was further reacted with sodium monochloroacetate to produce carboxymethyl cellulose.

Based on the preliminary result for the production of CMC using raw Jelutong, the highest DS value of CMC (0.237) was obtained when synthesis was carried out at a temperature of 55 °C and a reaction time of 3 hr. A maximum CMC (sago waste) DS value of 0.768 was obtained after 180 min of reaction time (Pushpamalar et al., 2006).

The concentration of sodium hydroxide is also one of the important factors for etherification reaction. The effect of sodium hydroxide concentration on the DS value was shown in Fig. 2 with the average SD of DS, RE, and product yield was 0.03, 3.73, and 3.54, respectively. The etherification process using 40% sodium hydroxide produced CMC with a DS value of 0.723 with 43.33% reaction efficiency and 165% product yield. Increased concentration of sodium hydroxide decreased the DS, RE, and product yield of CMC due to the increased yields of sodium glycolate that inactivates the sodium monochloroacetate (Palle, 2008; Joshi et al. 2015; Ab Rasid et al. 2021). Ahmed et al. (2018) reported that increasing the sodium hydroxide concentrations affected the yield of CMC as well as the DS value. This is because of the substitution of carboxymethyl groups during carboxymethylation where the carboxymethyl groups have higher molecular weight compared to hydroxyl group. Besides that, the selection of solvent medium will also affect the quality of CMC produced. The solvent increases the accessibility of the reactants in the etherification of the cellulose chain since isopropanol has a polarity less than water (Heydarzadeh et al., 2009).

Moreover, the increase in DS value is interrelated with the increase of hydrogen bonding between water and the carboxymethyl group and helps to bind a large amount of water (Fan et al., 2011). Furthermore, the DS value has a strong correlation with product yield where the higher the DS of CMC, the product yield also increased (Hong, 2013). Alabi et al. (2020) mentioned that the yield of CMC depends on the reaction temperature, the concentration of NaOH, and the amount of monochloroacetic acid applied during the synthesis process.

The DS of commercial CMC reported by Karatas and Arslan (2016) and Alabi et al. (2020) ranged from 0.5 to 1.5. Therefore, the DS of CMC Jelutong (0.723) obtained from this study falls within the accepted range of commercial CMC. When the DS value falls below 0.4, the CMC is swellable but insoluble in water. However, above this value, the CMC is fully soluble and the DS value increased when the hydro-affinity increased (Arshney et al. 2006; Alabi et al. 2020).

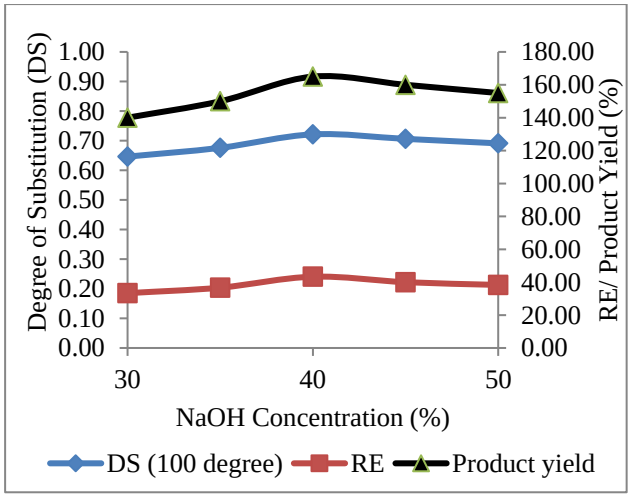


Fig. 2: Effect of Sodium Hydroxide Concentration on DS, RE and Product Yield of CMC from Jelutong

3.5 Morphology structure of carboxymethyl cellulose (CMC) from Jelutong using Scanning Electron Microscopy (SEM)

The CMC produced was further analysed using Scanning Electron Microscopy (SEM) to study its morphology structures. Fig. 3 shows the SEM micrographs of the CMC sample in comparison with raw and bleached Jelutong biomass to compare the change of morphology structure before and after conversion into CMC.

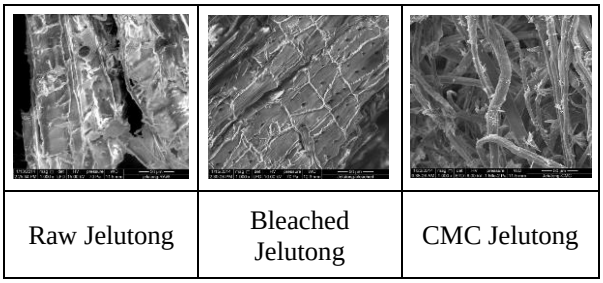
Raw and bleached Jelutong maintains the woody structure, and CMC with a DS value of 0.723 has a smooth surface with a structure like a rod shape same as reported by Ahemen et al. (2013). Etherification reaction to produce CMC from Jelutong has surface morphology structure changes from a woody structure to a smooth structure (Pushpamalar et al, 2006).

As compared to CMC jelutong, bleached jelutong showed a lot of empty pits. These empty pits were filled up with sodium monochloroacetate to become smooth surfaces as shown in the CMC jelutong morphology structure (Palle, 2008). Besides that, CMC jelutong produced is also comparable to CMC produced from other biomass from other researchers as shown in Fig. 4 and Table 3.

It showed almost similar morphology structure although it was produced from different biomass resources and the DS value fall within the accepted range of commercial CMC.

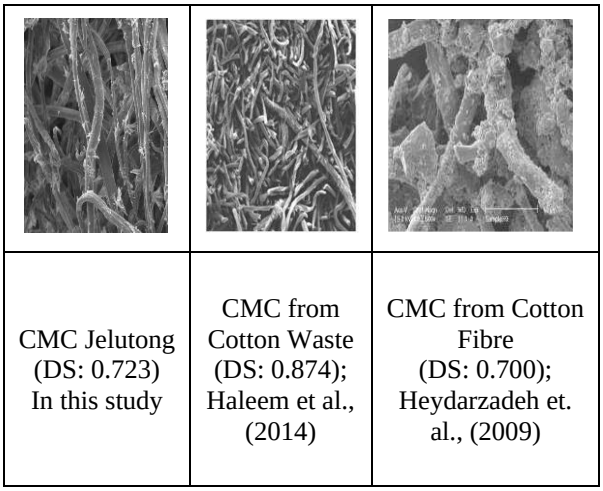
4.0 Conclusions

Carboxymethyl cellulose (CMC) was synthesised from Jelutong thinning biomass via the etherification process. It was found that the delignification process of the raw material which serves as a pretreatment stage is important to remove lignin and hemicellulose content. This process improved the percentage of alpha-cellulose contents of the delignified Jelutong up to 60 % through a modification of its chemical structure. Optimised conditions identified from this study gave CMC a DS value of 0.723 and RE of 43.33% by using delignified Jelutong (2 hr pulping using 10% sodium hydroxide) and reaction time 3 hr, at a temperature of 55 ˚C, 40% of sodium hydroxide, isopropanol as solvent medium and 3 g of sodium monochloroacetate. Modifications of cellulose structure into carboxymethyl cellulose improved its surface morphology compared to the raw material. Since the DS (0.7216) value of the synthesised CMC falls within the range of commercial CMC, it is therefore possible to use Jelutong thinning biomass as a feedstock for CMC production.



Raw Jelutong	Bleached Jelutong	CMC Jelutong

Fig. 3: SEM micrographs of Raw, Bleached and CMC Jelutong with magnification 1000×



CMC Jelutong (DS: 0.723) In this study	CMC from Cotton Waste (DS: 0.874); Haleem et al., (2014)	CMC from Cotton Fibre (DS: 0.700); Heydarzadeh et. al., (2009)

Fig. 4: Surface morphology structure of CMC produced from Jelutong and other biomasses

Table 3: Comparison of CMC produced from various type of biomass

Biomass type	DS value	References
Jelutong biomass	0.72	This study
M. paradisiaca (stalk)	0.28	Alabi et al. (2020)
T. diversifolia (stalk)	0.33	Alabi et al. (2020)
Palm kernel shell	0.31	Huang et al. (2017)
Miscanthus sinensis	0.35	Kimani et al. (2016)
Eichhornia crassipes	0.80	Kimani et al. (2016)
Cyperus papyrus	0.76	Kimani et al. (2016)
Baobab fruit shell	0.93	Ahmed et al. (2018)

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References

Ab Rashid, N. S., Mohamad Zainol, M., & Saidina Amin N. A. (2021). Synthesis and characterization of carboxymethyl cellulose derived from empty fruit bunch. *Sains Malaysiana, 50*(9), 2523–2535.

Ahemen, I,. Meludu, O., & Odoh, E. (2013). Effect of sodium carboxymethyl cellulose concentration on the photophysical properties of zinc sulfide nanoparticles. *British Journal of Applied Science & Technology 3*(4), 1228–1245. https://doi.org/ 10.9734/BJAST/2014/3803

Ahmed, A.A.Y., & Taiseer, H. M. (2018). Synthesis and characteristics of carboxymethyl cellulose from baobab (*Adansonia digitata* L.) fruit shell. *International Journal of Engineering and Applied Science*, *5*(12), 10. https://dx.doi.org/10.31873/IJEAS.5.12.02

Alabi, F., Labunmi, L., Olubode, A., Adebayo, A., Emmanuel, S. & Fadeyi, A. (2020). Synthesis and characterization of carboxymethyl cellulose from *Musa paradisiaca* and *Tithonia diversifolia*. *African Journal of Pure and Applied Chemistry*, *14*, 9–23. https://doi.org/ 10.5897/AJPAC2019.0821

Asl, S.A., Mousavi, M., & Labbafi, M. (2017). Synthesis and characterization of carboxymethyl cellulose from sugarcane bagasse. *Journal of Food Processing Technology*, *8*(8), 1000687. https://doi:10.4172/2157-7110.1000687

Arshney, V. K., Gupta, P. K., Naithani, S., Khullar, R., Bhatt, A., & Soni, P.L. (2006). Carboxymethylation of α-cellulose isolated from *Lantana camara* with respect to degree of substitution and rheological behavior. *Carbohydrate Polymers 63*(1), 40–45. https://doi.org/10.1016/j.carbpol.2005.07.001

Betts, W. B., Dart, R. K., Ball, A. S., & Pedlar, S. L. (1991). Biosynthesis and structure of lignocellulose. In W. B. Betts (Ed) *Biodegradation: Natural and Synthetic Materials* (pp. 139–155). Berlin, Germany Springer-Verlag.

Bono, A., Ying, P. H., Yan, F. N., Muei, C. L., Sarbatly, R., & Krishnaiah, D. (2009). Synthesis and characterization of carboxymethyl cellulose from palm kernel cake. *Advance in Natural and Applied Science 3*(1), 5–11.

Fan, L., Wang, L., Gao, S., Wua, P., Li, M., Xie, W., Liu, S., & Wang, W. (2011). Synthesis, characterization and properties of carboxymethyl kappa carrageenan. *Carbohydrate Polymers, 86*, 1167–1174. https://doi.org/10.1016/j.carbpol.2011.06.010

Haleem, N., Arshad, M., Shahid, M., & Tahir, M. A. (2014). Synthesis of carboxymethyl cellulose from waste of cotton ginning industry. *Carbohydrate Polymers*, 113: 249–255. https://doi.org/10.1016/j.carbpol.2014.07.023

Ambjörnsson, H. A., Schenzel, K., & Germgård, U. (2013). Carboxymethyl cellulose produced at different mercerization conditions and characterized by NIR FT raman spectroscopy in combination with multivariate analytical methods. *Bioresources, 8*(2), 1918–1932. https://doi.org/10.15376/BIORES.8.2.1918-1932

Heydarzadeh, H. D., Najafpour, G. D., & Nazari-Moghaddam, A. A. (2009). Catalyst-free conversion of alkali cellulose to fine carboxymethyl cellulose at mild conditions. *World Applied Sciences Journal 6*(4), 564–569.

Hong, K. M. (2013). *Preparation and characterization of carboxymethyl cellulose from sugarcane bagasse*. [Bachelor's Degree Thesis, Universiti Tunku Abdul Rahman (UTAR)]

Huang, C. M. Y., Chia, P., Lim, S. S., Nai, J. Q., Ding, D. Y., Seow, P. B., Wong, C. W., & Chan, W. C. (2017). Synthesis and characterisation of carboxymethyl cellulose from various agricultural wastes. *Cellulose Chemistry and Technology, 51*(7-8), 665–672.

Hutomo, G. S., Marseno, D. W., & Supriyanto, S. A. (2012). Synthesis and characterization of sodium carboxymethylcellulose from pod husk of Cacao (*Theobroma cacao* L.). *African Journal of Food Science, 6*(6): 180–185. https://doi.org/10.5897/AJFS12.020

Jeyanny, V., Zuhaidi Y. A., Suhaimi, W. C., & Amir, S. K. (2010, August 1–6). *Site suitability assessment for sustainable forest plantation establishment of Dyera costulata in a West Malaysian tropical forest.* 19th World Congress of Soil Science Soil Solutions for a Changing World, Brisbane, Australia.

Jung, S. J., Kim, S. H., & Chung, I. M. (2015). Comparison of lignin, cellulose, and hemicellulose contents for biofuels utilization among 4 types of lignocellulosic crops. *Biomass Bioenergy 83*, 322–327. https://doi.org/10.1016/j.biombioe.2015.10.007

Kimani, P., Kareru, P., Madivoli, S., Kairigo, P. K., Maina, E., & Rechab, O. (2016). Comparative Study of Carboxymethyl Cellulose Synthesis from Selected Kenyan Biomass. *Chemical Science International Journal 17*, 1–8. https://doi.org/10.9734/CSJI/2016/29390

Kucharska, K., Rybarczyk, P., Hołowacz, I., Łukajtis, R., Glinka, M., & Kaminski, M. (2018). Pretreatment of lignocellulosic materials as substrates for fermentation processes. *Molecules 23*(11), 1–32. https://doi.org/ 10.3390/molecules23112937

Mat Soom R, Wan Hassan WH, Md Top AG and Hassan K. 2006. Thermal properties of oil palm fiber, cellulose and its derivatives. *Journal of Oil Palm Research, 18*, 272–277.

Mohamad Zainol, M., Ab Rasid, N. S., Asmadi, M., & Saidina Amin, N. A. (2021). Carboxymethyl cellulose synthesis from treated oil palm empty fruit bunch using ionic liquid and hydrogen peroxide. *ASEAN Engineering Journal*, *11*(4), 80. 1https://doi.org/0.11113/aej.v11.17866

Palle, I. (2008). Carboxymethylation of cellulose from kenaf (*hibiscus cannabinus* l.) core for hydrogel production. [Master's Thesis, Universiti Putra Malaysia]

Parid, D. M., Abd Rahman, N. A., Baharuddin, A. S., Mohammed, M. A. P., Mat Johari, A., & Abdul Razak, S. Z. (2018). Synthesis and characterization of carboxymethyl cellulose from oil palm empty fruit bunch stalk fibres. *BioResources, 13*(1), 535–554. https://doi.org/10.15376/biores.13.1.535-554

Tuan Mohamood, N. F. A. Z., Abdul Halim, A. H., & Zainuddin, N. (2021). Carboxymethyl Cellulose Hydrogel from Biomass Waste of Oil Palm Empty Fruit Bunch Using Calcium Chloride as Crosslinking Agent. *Polymers*, *13*(23), 4056. https://doi.org/10.3390/polym13234056.

Pinto, E., Wilberforce, A., Patrick, B., Gershon, A., Yen Adams, S. N., Michael, F., Hassan, K., Kwame, S., Caspar, A., Samuel, E., & Mizpah, R. (2022). Cellulose processing from biomass and its derivatization into carboxymethylcellulose: A review. *Scientific African*, *15*, e01078. https://doi.org/10.1016/j.sciaf.2021.e01078

Pushpamalar, V., Langford, S. J., Ahmad, M., & Lim, Y. Y. (2006). Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *Carbohydrate Polymers*, *64*, 312–318. https://doi.org/10.1016/j.carbpol.2005.12.003

Rachtanapun, P., Luangkamin, S., Tanprasert, K., & Suriyatem, R. (2012). Carboxymethyl cellulose film from durian rind. *LWT - Food Science and Technology*, *48*(1), 52–58. https://doi.org/10.1016/j.lwt.2012.02.029

Rahman, M. S., Mondal, M. D., Yeasmin, S., Sayeed, M. D., & Hossain, M. D. (2020). Conversion of lignocellulosic corn agro-waste into cellulose derivative and its potential application as pharmaceutical excipient. *Processes*, *8*(711). https://doi.org/10.3390/pr8060711.

TAPPI: T 203 cm-09. (2009). Alpha-, beta- and gamma-cellulose in pulp. 1–5.

TAPPI: T 204 cm-07. (2007). Solvent extractives of woof and pulp. 1–4.

TAPPI: T222 om-11. (2011). Acid-insoluble lignin in wood and pulp.

Tasaso, P. (2015). Optimization of reaction conditions for synthesis of carboxymethyl cellulose from oil palm fronds. *International Journal of Chemical Engineering and Applications* *6*(2), 101–104. https://doi.org/10.7763/IJCEA.2015.V6.460

Germgård, U., & Hedlund, A. (2006*). The influence of wood and dissolving pulp properties of carboxymethyl cellulose reaction.* [Paper presentation]. 2006 Engineering, Pulping, & Environmental Conference, Karlstad University.

Wise, L. E., Murphy, M., & D'addieco, A. A. (1946). Chlorite holocellulose: Its fractionation and bearing on summative wood analysts and on studies on the hemicelluloses. *Paper Trade Journal*, *122*(2), 35–43.