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Synthesis Carboxyl Methyl Cellulose (CMC) with Addition Method from Durian Seed

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ABSTRACT

Carboxy Methyl Cellulose (CMC) is a compound made from durian seed, where durian seeds is converted into the powder by the method of addition of methanol, propanol and water. Three consecutive process involves are the process of alkalization, carboxymethylamine, neutralization in the process of synthesis CMC. The first process are made by reacting NaOH and $ClCH_2COONa$ with NaOH 22; 32.5 g and 20 ; 32 g $ClCH_2COONa$ respectively. Acetic acid is added is used in the neutralization process, during the heating process in the oven. The overall results for each degree of substitution; viscosity; pH; water content; NaCl concentration; purity and yield of 0.76 - 0.77; 6-8 cP; 8; 8.7 to 17.7 %; 2.06 to 2.24 ; 97.76 to 97.96 % ; and 93.5 to 97.5 % respectively. Based on the research results obtained, it can be concluded that the CMC is of good quality as a filler.

Keywords: CMC, Addition Method, Alkalization, Carboxymethylization

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INTRODUCTION

Durian seed is part of a durian fruit that is not consumed by most people as slimy and cause itching on the tongue. Yet seen from the nutritional content, durian seed has sufficient potential as a source of nutrition, which contains proteins, carbohydrates, fat, calcium and phosphorus. Therefore, durian seeds can be used as an alternative material in the manufacture of CMC and can helping to clean environment [4, 6].

The main factor to consider in the manufacture of CMC is alkalization and carboxymethylamine, because it determines the characteristics of the resulting CMC [13]. Alkalization performed before carboxymethylamine using NaOH which aims to activate groups OH in cellulose molecules and function as developers. This will facilitate the deployment of cellulosic diffusion carboxymethylamine reagent. In the process used reagent Carboxymethylamine monochloroacetate acid or sodium monochloroacetate and this reagent is usually used in practice [3].

The amount of sodium monochloroacetate used will affect the substitution of the anhydroglucose unit in the cellulose. The increasing of the amount alkali used may increase the amount of salt dissolved monochloroacetate thus simplifying and accelerating the diffusion of salt monochloroacetate into the reaction center that is a hydroxy group [14].

Considering the role of both reagents the second reagent composition either alkalization or carboxymethylamine in this process will determine the quality of the resulting CMC [1]. As the development of the industry, said many factories producing Cellogen CMC that lists the degree of substitution [DS], pH and viscosity as the characteristics of the product [5]. Indonesian Industrial Standard lists nine kinds of quality requirements every CMC for first quality and second quality. Conditions to be met largely depends on the intended use for the purposes of food or non-food industry [9, 12].

MATERIALS AND METHODS

TOOLS AND MATERIALS

In this research use Durian fruits, extract powder of Durian seed, propanol, metanol, aquadest, NaOH, Natrium Monochloroacetic, H_2SO_4, buffer solution (pH 7), PP indicators, etanoat acid, $AgNO_3$ and K_2CrO_4. Tools in this research such as samples grinder, sieve size of 100 mesh, analytical balance brand Sartorius, oven brands Memmert, set stirrer Brands Heidolph, Type RZR 1, three neck flask volume 1 L, funnel glass, beakers, measuring cups, Buchner funnel and the vacuum pump and furnace brand Heraeus.

Preparation of materials (creation production of durian seed power)

Durian seeds (as shown in figure 1) are dried in the open air and then grinded and sieved to 100 mesh size. Furthermore, the moisture content is determined by weighing 2 grams (W1) The durian seeds in a weighing bottle, put into the oven for 4 hours at a temperature of 105°C then inserted in eksikator and weighed until the weight remains (W2) (7, 12).

$$\text{Water Percentation} = \{(W_1 - W_2) / W_1\} \times 100\ \%$$

(a) (b) (c)

Figure 1. Durian (*Durio zibethinus*) fruit (a), internal morphology of Durian fruit (courtesy of www.Agropustaka.com) (b) and Durian seed (c)

The process of alkalization and carboxymethylamine

20 grams of dry weight of durian seed powder was added to a 3-neck flask was placed in a water bath and then $CH_3CHOHCH_3$ 400 mL added, 50 mL of CH_3OH, 50 mL of distilled water (aquadest) were added and stirred for 10 minutes. Then 30% NaOH solution (22 g NaOH) added dropwise and this alkalization process lasted for 1 hour at a temperature of 24°C. After completion of the process followed by addition it $ClCH_2COONa$ carboxymethylamine by adding as much as 20 g little by little. This process lasts for 3.5 hours at a temperature of 55°C. During both of these processes take place stirrer still turning (13).

The process of neutralization and drying

After process of Carboxymethylamine is complete, the stirrer is turned off and then the mixture is transferred into a beaker and measured pH. Furthermore CH_3COOH wa added to pH neutral and decanted. The residue obtained added 200 mL CH_3OH and stirred then filtered using a vacuum pump. Finally, wrapped in aluminum foil and dried in an oven for 4 hours at a temperature of 60°C. CMC that has been dried, crushed and stored in a closed place (13).

Figure 2. Extraction of Durian seed for synthesis CMC

Determination of the degree of substitution (DS)
Prior to the degree of substitution is determined, it is necessary to know in advance the water content of the CMC, resulting in the determination of the degree of substitution, based on the dry weight. Weighed 0.7 g (dry weight) CMC on filter paper in the cup, then the paper containing CMC the wrapped. CMC cup containing the sample is inserted into the furnace for 5 hours at a temperature of 75^oC. After that it was moved into the oven and then inserted into eksikator for 12 hours at a temperature of 100^oC and then put into eksikator for 2 hours . Furthermore, the sample is placed in a beaker, added 35 ml of H_2SO_4 0.1 N, 250 mL of distilled water (aquadest) and then boiled for 30 minutes. The samples were cooled added Phenolphtalein indicator then titrated with 0.1 N NaOH while stirring slowly until the color changes from colorless to pink (5).

The degree of substitution (DS) is calculated by :

DS = (162 x A) / (10.000 – 80A)

A = (af-bf1) / (Mass of dried sample in gram) – alkality ; or
A = (af-bf1) / (Mass of dried sample in gram) + acidity

Description :
A = acidity/alkalinity
a = volume of 0.1 N H_2SO_4 used
f = factor of 0.1 N H_2SO_4
b = volume of 0.1 N NaOH required
f1 = factor of 0.1 N NaOH
162 = net increase molecular weight anhydroglucose unit for each unit CMC group added
10,000 = average - average degree of polymerization of the cellulose

Separately, alkalinity or acidity of the sample is measured in the following manner :
1 gram of dry CMC is weighed in the beaker , then added 30 mL of 0.1 N H_2SO4 and 200 mL of distilled water is heated for 10 minutes. Once cool added indicator PP and I with 0.1 N NaOH titration (NaOH required = S mL) . Test form (without CMC) carried out at the same time (NaOH required = B ml). Furthermore alkalinity or acidity calculated by the following formula :

$$\text{Acidity (alkalinity)} = \{(B - S) \times f_1\} / \text{dried sample}$$

Measurement of pH CMC 1%
1 gram of dry CMC is weighed, added 100 mL of distilled water and then heated to a temperature of 70^oC while stirring until dissolved and after cold measured pH (5).

Viscosity measurements CMC solution 2%
4,4 gram of dry CMC is weighed included in a beaker of distilled water and then added that the amount calculated using the formula:

$$\text{Volume (mL) of distilled water} = \text{sample weight (g)} \times \{(98 - \text{water content})\}/ 2$$

After distilled water added, the mixture shaken for 30 minutes and poured into a beaker. Viscosity is inserted and then rotated at 30 rpm for 3 minutes followed by readings scale (5).

Determination levels of NaCl
1 gram of dry CMC is weighed inserted into Erlenmeyer and diluted with 200 mL of distilled water (13). The solution is then titrated with 0.1 N AgNO3 and indicators K_2CrO_4 5%.

NaCl concentration (%) = (0.5845 x f x vol $AgNO_3$) / Dry sample weight (g)

Purity determination of CMC
CMC purity is calculated as follows (13):
Purity = 100% -% NaCl.

Determination of yield
Yield = (Weight obtained/Weight theory) x 100%

RESULTS AND DISCUSSION

From laboratory analysis has been done, obtained the following results:

Tabel .1. The result of CMC analysis (2, 6).

No	Parameter	$ClCH_2COONa$ (g)	NaOH (g)	$ClCH_2COONa$ (g)	NaOH (g)
		20	22	32	32,5
1	Degree of substitution	0,77		0,76	
2	pH	8		8	
3	Viscosity (cP)	6		8	
4	Water content (%)	8,7		17,7	
5	NaCl concentration (%)	2,06		2,24	
6	Purity (%)	97,96		97,76	
7	Yield (%)	97,5		93,5	

Based on the results of this research in Table 1 on the addition of NaOH 30% by 22 g occur an increase in the degree of substitution. According to Ott & Spurlin, the addition of NaOH will increase the degree of substitution, this would mean the addition of 22 g NaOH have developed a cellulose optimally. If NaOH is added over 22 g namely 32.5 g NaOH reacts with the rest of $ClCH_2COONa$ forming $HOCH_2COONa$ (sodium glycolate) and NaCl (sodium chloride), which resulted in the decline in the degree of substitution.

The reaction according to the equation (8, 13) ;

$$ClCH_2COONa \rightarrow HOCH_2COONa + NaOH + NaCl$$

At carboxylation process with the addition of $ClCH_2COONa$, obtained the degree of substitution which decreases with increasing $ClCH_2COONa$ and reached a maximum on the addition of NaOH and $ClCH_2COONa$ combination of 22 grams and 20 grams which is 0.77. In terms of quality, the greater the degree of substitution rates, the better the quality CMC because the greater solubility in water.

Based on applicable standards, the degree of substitution is in the price range between 0.7 to 1.2 and the pH of a 1% solution between 6.0 to 8.0 thus the results can be accepted. Judging price of viscosity, under the same conditions as above obtained price of 6 cP, these include the group with low viscosity CMC in relation to pH, CMC results of its research base. This trait is highly recommended that the viscosity is not increased that it becomes difficult to mix due to the formation of deposits. For NaCl concentration, in terms of changes NaOH is added, there is a change in line with changes in the degree of substitution. If the review of the changes $ClCH_2COONa$ NaCl concentration further increase due to higher $ClCH_2COONa$, because NaCl is a by product of the reaction due to the formation of excess reagent CMC added. CMC purity results showed an increase in the addition of NaOH but decreased when $ClCH_2COONa$ further, it is a result of the increasing number of NaCl produced. The yield of the two samples produced from CMC is more than 90% (8, 13).

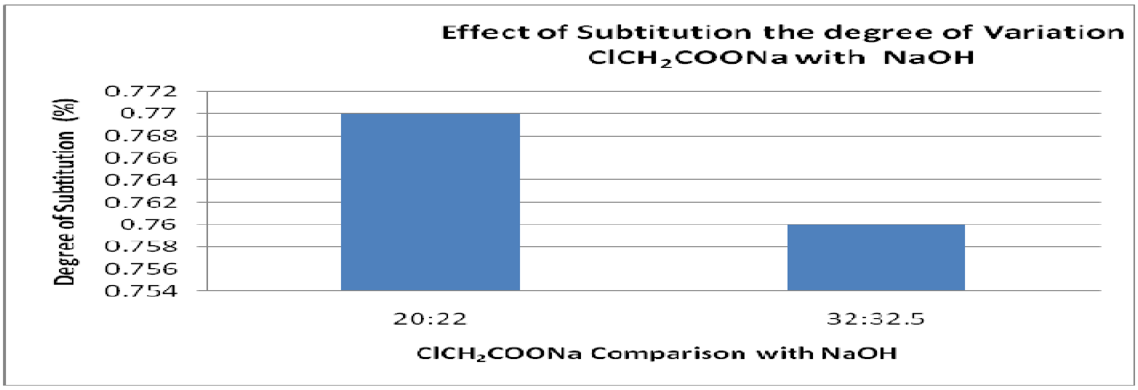

Figure 3. Effect of Substitution The degree Variation $ClCH_2COONa$ with NaOH

Effect of Substitution The Degree Variation $ClCH_2COONa$ with NaOH

Based on Figure 3 can be seen the influence of the degree of substitution by comparison $ClCH_2COONa$ with NaOH, the addition of NaOH over 22 g can reduce the degree of substitution due to the addition of NaOH 22 g has developed a cellulose optimally and the rest of the NaOH reacts with $ClCH_2COONa$ forming $HOCH_2COONa$ (sodium glycolate) and NaCl (sodium chloride), which resulted in the decline in the degree of substitution. And in terms of the degree of sustitusi the higher the degree of substitution of the CMC quality the better since the greater solubility in water. Under the applicable standard degree of substitution is in the price range from 0.7 to 1.2 (11, 14).

Effect of pH Variation $ClCH_2COONa$ with NaOH

Based on Figure 4 can be seen the effect of pH by comparing ClCH2COONa with NaOH, a second addition of NaOH and $ClCH_2COONa$ having a pH of 8, this resulted in CMC is alkaline. Under the applicable standard price in the range of pH 6-8 (11, 14).

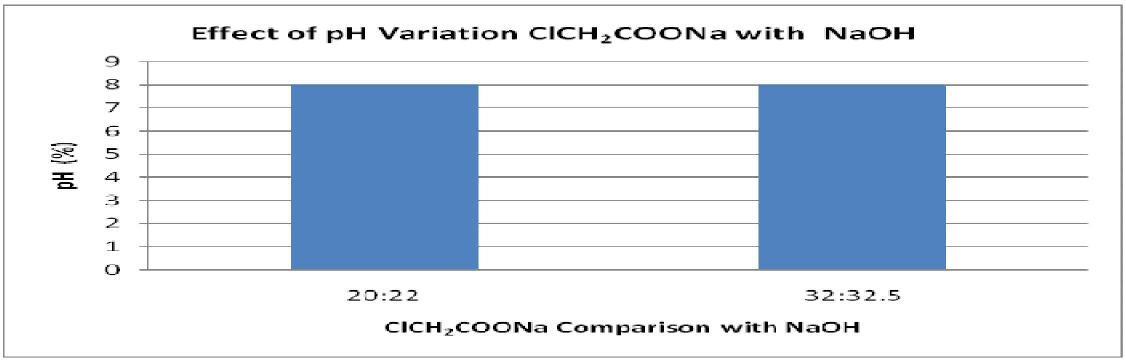

Figure 4. Effect of pH Variation $ClCH_2COONa$ with NaOH

Effect of Viscosity Variation $ClCH_2COONa$ with NaOH with NaOH

Based on Figure 5 can be seen the effect of viscosity by comparing $ClCH_2COONa$ with NaOH, the addition of more than 22 g NaOH can increase viscosity due to the addition of NaOH as closely related to pH is 6 cP to 8 cP, including CMC alkaline. This trait is highly recommended that the viscosity is not great increased that it becomes difficult to mix due to the formation of deposits (11, 14).

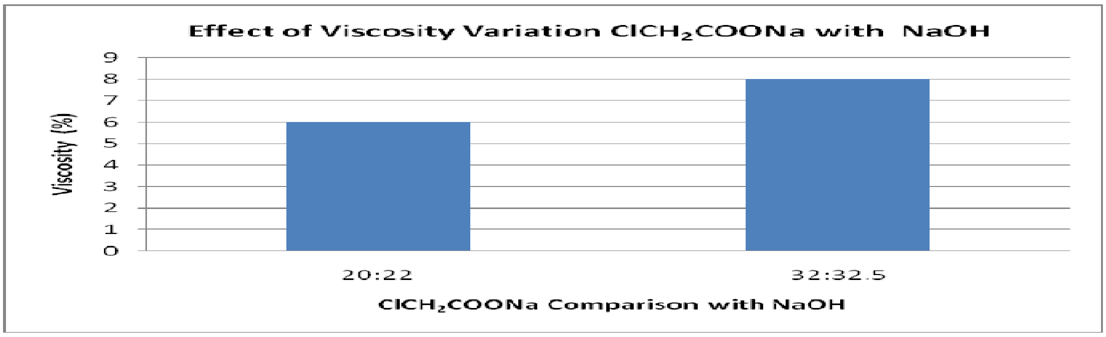

Figure 5. Effect of Viscosity Variation $ClCH_2COONa$ with NaOH

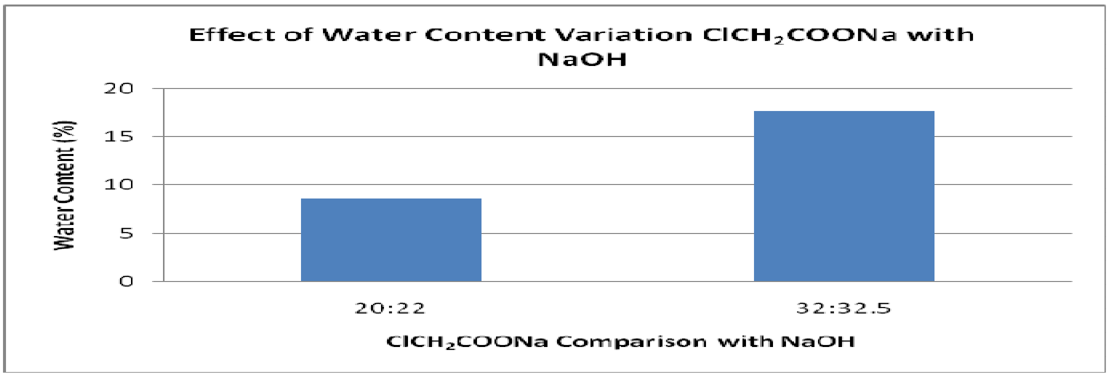

Figure 6. Effect of Water Content Variation $ClCH_2COONa$ with NaOH

Effect of Water Content Variation $ClCH_2COONa$ with NaOH

Based on Figure 6 can be seen the effect of water content by comparing $ClCH_2COONa$ with NaOH, the addition of more than 22 g NaOH can raise water levels due to the addition of NaOH as closely related to pH is 2.06 to 2.24%.

The high water content greatest effect on endurance CMC produced, so the lower the water content, the better the resulting CMC (11, 14).

Effect of Levels NaCl Variation $ClCH_2COONa$ with NaOH

Based on Figure 7 can be seen the effect of NaCl concentration by comparing ClCH2COONa with NaOH, the addition of more than 22 g NaOH can raise the levels of NaCl as NaCl concentration, in terms of the addition of NaOH is added, there is a change in line with changes in the degree of substitution. If the review of the changes $ClCH_2COONa$ NaCl concentration further increase due to higher $ClCH_2COONa$, because NaCl is a by product of the reaction due to the formation of excess reagent CMC added (11, 14).

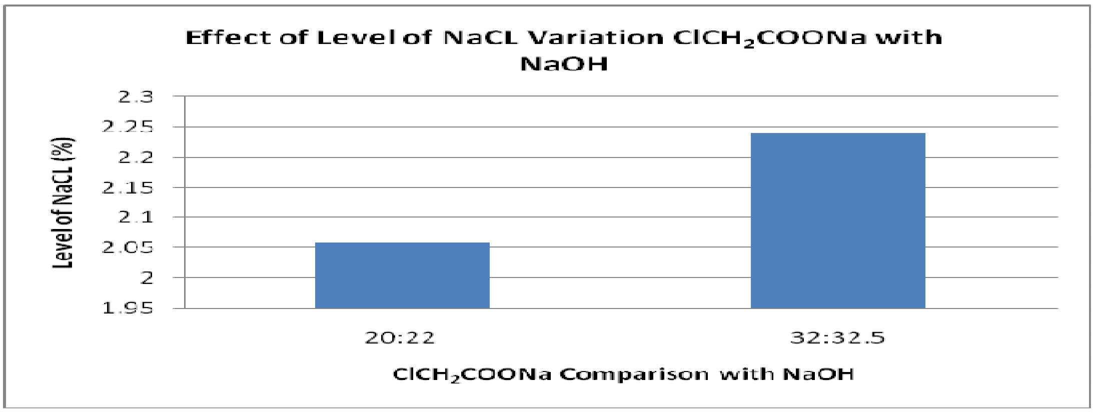

Figure 7. Effect of Levels NaCl Variation $ClCH_2COONa$ with NaOH

Effect of Purity Variation $ClCH_2COONa$ with NaOH

Based on the Figure 8 can be seen the effect of purity by comparing $ClCH_2COONa$ with NaOH, the addition of more than 22 g NaOH may raise purity. Because of the purity, in terms of the addition of NaOH is added, there is an increase in line with the levels of NaCl. CMC purity results showed an increase in the addition of NaOH but decreased when $ClCH_2COONa$ increased, it is a result of the increasing number of NaCl produced (8, 13).

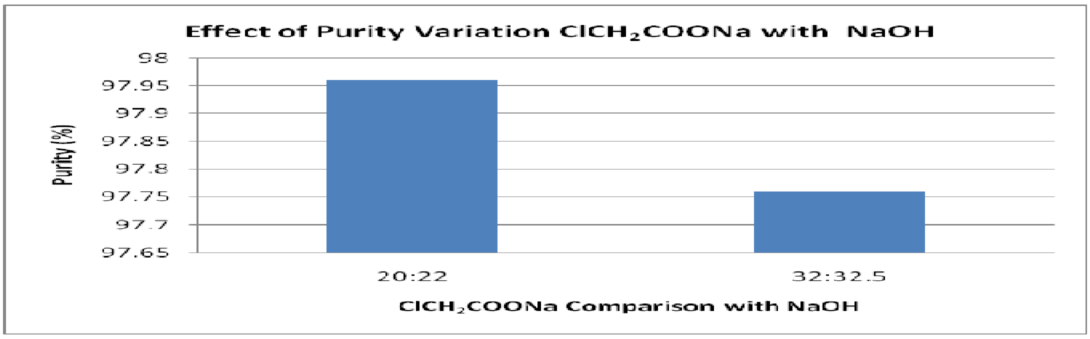

Figure 8. Effect of Purity Variation $ClCH_2COONa$ with NaOH

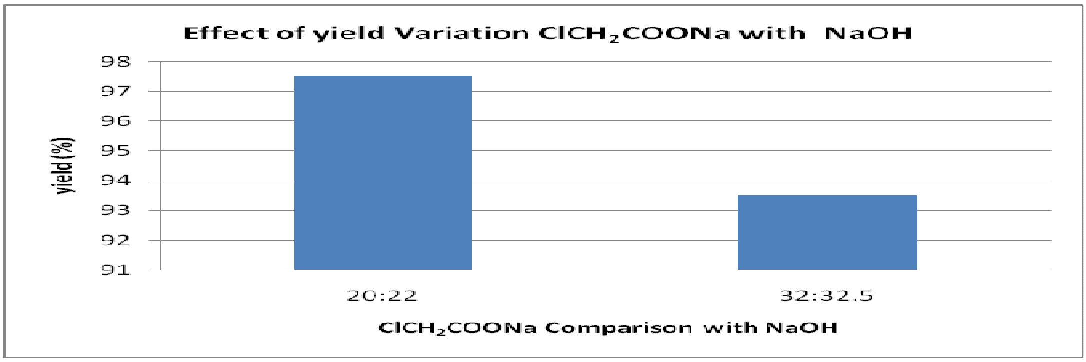

Figure 9. Effect of yield Variation $ClCH_2COONa$ with NaOH

Effect of yield Variation $ClCH_2COONa$ $ClCH_2COONa$ with NaOH

Based on the Figure 9 can be seen the effect on the yield of 30% NaOH addition of 22 g of an increase yield. If NaOH is added over 22 g is 32.5 g, the yield may decrease (8, 13).

CONCLUSION

From the results and discussion on this study can be summarized as ; From the composition ratio of NaOH and $ClCH_2COONa$ can be concluded that the ratio of sodium hydroxide 22 g and $ClCH_2COONa$ that 20 g produces good quality of CMC because this CMC already can be applied in the manufacture of detergent, paint ceramic textiles and food as a thickener, stabilizer emulsion or suspension and binder.

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