Carboxymethyl cellulose synthesis using durian rind

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Abstract

Durian rind is used to synthesis carboxymethyl cellulose (CMC) in this research. The aim of this work was to find the appropriate the conditions for cellulose extraction and CMC synthesis. Two methods of cellulose extraction from durian rind, the acid-base treatment, and base treatment were compared. From the study found that the base treatment is more efficiency in lignin removal than the acid-base treatment. After-acquired the cellulose, CMC can be produced using 2 steps: alkalization and carboxymethylation step. Alkalization is the reaction between cellulose and sodium hydroxide in isopropyl alcohol-water mixture. The concentration of sodium hydroxide (NaOH) in this step was study in the range of 10 to 30 %w/v. In carboxymethylation step, the monochloroacetic acid (MCA) was added to substitute the carboxymethyl group. Variation of reactants mole ratio (mol NaOH: mol MCA) and time in carboxymethylation will be studied to find appropriate condition for CMC synthesis from durian rind. The obtained CMC was characterized by FT-IR and the degree of substitution (DS). The appropriate conditions to the synthesis of CMC using durian rind was the reactant ratio 1:1 for 3 hours to obtained CMC with the DS of 1.11.

Keywords: Carboxymethyl cellulose (CMC), alkalization, carboxymethylation

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บทคัดย่อ

ในงานวิจัยนี้เปลือกทุเรียนได้ถูกนำมาศึกษาเพราะว่าทุเรียนเป็นผลผลิตทางการเกษตรหลักของไทยทำให้มีเปลือกทุเรียนเหลือทิ้งจำนวนมากทุกปี จุดประสงค์ของงานวิจัยนี้คือหาสภาวะที่เหมาะสมที่ในการสกัดเซลลูโลสและสังเคราะห์ซีเอ็มซีจากเปลือกทุเรียน จากการเปรียบเทียบวิธีการสกัดเซลลูโลสจากเปลือกทุเรียน 2 วิธีคือการใช้กรดซัลฟูริก-โซเดียมไฮดรอไซด์ และการใช้โซเดียมไฮดรอกไซด์เพียงอย่างเดียว พบว่า การสกัดโดยใช้โซดียมไฮดรอกไซด์เพียงอย่างเดียวมีประสิทธิภาพในการกำจัดลิกนินมากกว่าการใช้ทั้งกรดซัลฟูริกและโซเดียมไฮดรอกไซด์ หลังจากได้เซลลูโลส ซีเอ็มซีสามารถผลิตได้ด้วย 2 ขั้นตอนคือปฏิกิริยาอัลคาไลเซชั่นและคาร์บอกซิเมทิลเลชั่น อัลคาไลเซชั่นคือการทำปฏิริยาระหว่างเซลลูโลสกับโซเดียมไฮดรอกไซด์ ในสารละลายไอโซโพรพิลแอลกอฮอล์และน้ำ ในขั้นตอนนี้ได้ศึกษาความเข้มข้นของโซเดียมไฮดรอกไซด์ที่ใช้ทำปฏิกิริยาในช่วง 10-30 ร้อยละน้ำหนักต่อปริมาตร ปฏิกิริยาคาร์บอกซิเมทิลเลชั่นมีการเติมกรดคลอโรอะซิติก (MCA) เพื่อแทนที่หมู่คาร์บอกซิเมทิล โดยได้ศึกษาเปลี่ยนแปลงอัตราส่วนโมลของสารตั้งต้น (โมลNaOH: โมลMCA) และเวลาในการทำปฏิกิริยาคาร์บอกซิเมทิลเลชั่น ซีเอ็มซีที่ได้ระบุคุณลักษณะด้วย FT-IR, ระดับการแทนที่หมู่ (DS) และปริมาณโซเดียมคลอไรด์ งานวิจัยจะศึกษาหาภาวะที่เหมาะสมในการผลิตซีเอ็มซีจากเปลือกทุเรียน พบว่าการทำปฏิกิริยาโดยใช้อัตราส่วนโมลของสารตั้งต้นเป็น 1:1 ทำปฏิกิริยา 3 ชั่วโมงสภาวะที่เหมาะสมที่สุดในการสังเคราะห์ซีเอ็มซีจากเปลือกทุเรียน ซึ่งได้ระดับการแทนที่หมู่เท่ากับ 1.11

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CHAPTER I
INTRODUCTION

1.1 Background

Thailand locates on the fertile floodplain area, which suited for cultivation about 47 percent of all area in Thailand used for agriculture [1]. It affects a lot of agricultural residues is generated. A large amount of waste from agricultural sector can be converted to carbon sources for renewable energy such as biodiesel, bioethanol or biogas in heat and power generation. Moreover, residues from agriculture can be used in bioplastic production due to its structure that contains plenty of cellulose, which is a natural polymer.

At the present, a large amount of waste from plastic usage was produced around 10,000 ton per day in Thailand [2]. It is continuously increasing because plastic residues are difficult to degrade or take a long time to decompose. Bioplastic become interesting material because it can be made from natural material, which contains cellulose. This bioplastic material can be decomposed in 120 days compared to petroleum plastic that used 450 years to decompose and this bioplastic material is environmentally friendly. There are many types of bioplastics in present. Starch-based plastics that are about 50 percent of bioplastic. It is produced from natural starch such as cassava or corn and sugar. Another type of bioplastic which is interesting such as Polylactic acid (PLA). It is produced from fermentation of corn starch or sugar canes with microorganism and converts to lactic acid [3]. But the disadvantage of the bioplastic is high production cost. Therefore, the agricultural waste is used in the bioplastic production to decrease production cost, especially, the bioplastic production from carboxymethyl cellulose (CMC) obtains from the conversion of agricultural waste. CMC is one of the derivatives of cellulose, which obtains from carboxymethylation of cellulose. The major advantages of CMC are its solubility in water compared to normal cellulose that cannot dissolve in water. Moreover, when CMC is used in the bioplastic production, it decomposes in 24 hours. CMC from the agricultural waste in Thailand produces from durian rind, bagasse, water hyacinth etc. But the bioplastic production from CMC must add flour, sticky rice flour [4] for efficiency in forming. In this research, the focus is on the synthesis of CMC from durian rind and find optimum condition for CMC synthesis from durian rind.

1.2 Objectives

1) To find appropriate condition for cellulose extraction from durian rind.
2) To find appropriate condition for CMC synthesis from durian rind.

1.3 Scopes of Work

1) Study methods for extract the cellulose from durian rind: acid-base treatment and base treatment.
2) Study important parameters, which affect the CMC synthesis
    1.1) Reactant ratio of NaOH: Monochloroacetice acid (mol/mol) : 1:1, 2:1, 4:1 and 1:2
    1.2) Time for carboxymethylation (h): 3, 6

CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is a derivative of cellulose, which obtains from converting the structure and some properties of cellulose by substitute carboxymethyl group (-CH_2COO-) instead of a hydrogen atom in the hydroxy group as shown in figure 2.1. Generally, cellulose is insoluble in water but the conversion of cellulose to CMC will improve solubility in water of the cellulose in both hot and cold water. Because the substitution of a carboxymethyl group, this changes the polarity of the molecule of cellulose from non-polar molecule to polar molecule. Therefore, CMC is soluble in water, which is a polar molecule.

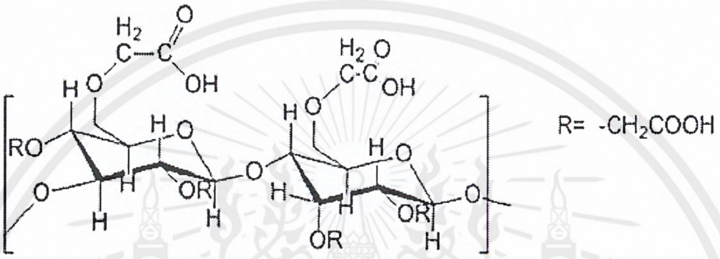


Figure 2.1 Structure of CMC [5].

2.1.1 Physical properties

CMC is white or cream powder, odorless and tasteless. It is insoluble in organic solvents such as methanol, alcohol, diethyl ether, acetone, chloroform, and benzene but soluble in water. The dissolution of CMC is improved by slowly adding CMC into the solvent during stirring [6].

The degree of substitution (DS) indicates the substitution of carboxymethyl group in the structure of cellulose. DS is an important factor that affects water solubility and the viscosity of carboxymethyl cellulose. In general, when the viscosity is in the range of 25-50 Pa•s. DS equals to 0.3, it miscible in alkaline while DS is more than 0.4, it miscible in water. With the rise of DS, the transparency of solution improves accordingly [7]. The maximum theoretical degree of substitution, which possibly occurs in CMC equals to 3. Not only the degree of substitution but also average chain length or degree of polymerization (DP) affects the characteristics of CMC solution because it is a long chain polymer. The molecular weight of the polymer is limited by average chain length and degree of substitution. As molecular weight increases, the viscosity of CMC solutions increases rapidly [8]. The pKa value of CMC was determined to be 3.2 [9].

2.2 Cellulose

Cellulose ($(C_6H_{10}O_5)_n$) is a linear polysaccharide, which contains more than 10,000 cellobiose subunits are linked with β-(1-4) glycosidic bond. Generally, cellulose is found in the cell wall of agricultural residue, or lignocellulose material because the cell wall of the plant consists of three main components, which are cellulose, hemicellulose, and lignin. Cellulose is surrounded by hemicellulose and lignin in the cell wall and it contains both crystalline and amorphous region as shown in figure 2.2 [10].

In crystalline cellulose, cellulosic chains are arranged into parallel microfibrils compacted into dense hydrogen-bonded fibers. This high-density results in a three-dimensional structure that is virtually impermeable to enzymes and, in most cases, even water. Naturally amorphous cellulose)or crystalline cellulose that is made amorphous via pretreatment(, lacks the same parallel fiber structure and the dense hydrogen bonding found in crystalline cellulose. This results in a less dense matrix with the more accessible surface area) and end groups(, thereby making it more susceptible to enzymatic degradation. While some enzymes specialize in attacking internal cellulose structure, others attack either the reducing or nonreducing ends of cellulose fibers [11].

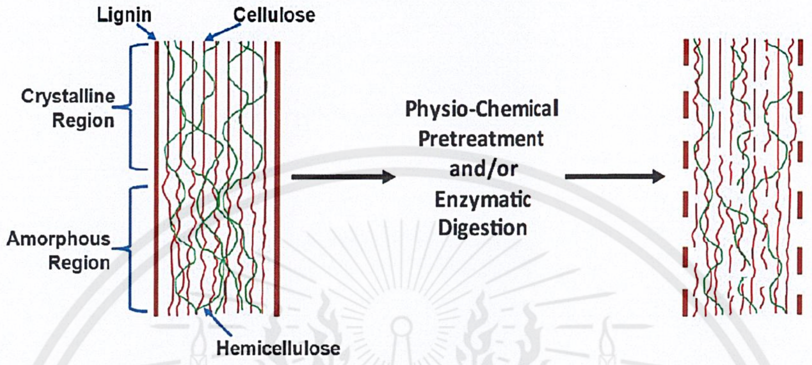


Figure 2.2 Lignocellulose structure before and after pretreatment [11].

Cellulose can separate into 2 categories based on configuration, alpha and beta cellulose as shown in figure 2.3 and 2.4 [12]. Alpha cellulose is prepared from various materials and different chemical method. Some cases, alpha cellulose is produced from mixed starch such as a mixture of starch, beta-glucan from oats, barley, and yeast or from polysaccharides in milk protein etc. In several countries, the alpha cellulose is synthesized from standing timber, pine tree, and eucalyptus tree. In contrast, the glucose monomers of cellulose are all in the β configuration, making every glucose monomer "upside down" with respect to its neighbors [12].

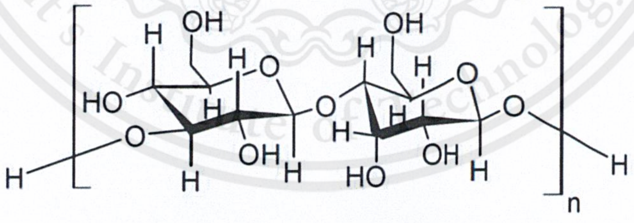


Figure 2.3 Structure of alpha cellulose

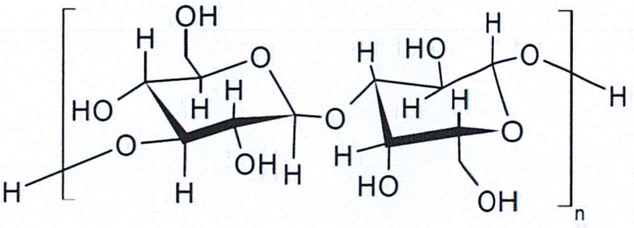


Figure 2.4 Structure of beta cellulose

2.2.1 Cellulose Extraction

Before converting agricultural residues to CMC, cellulose must be extracted from another component. There are two methods usually use in cellulose extraction, which are physical treatment and chemical treatment. Physical treatment includes mechanical (grounding, milling), gamma irradiation, ultrasound, and microwave. Another one is chemical treatment consists of acid and alkaline pretreatment. The cellulose and lignin are removed with alkaline pretreatment. The hemicellulose is removed with acid treatment. Sometimes, to eliminate others compound from cellulose, the agricultural residues may be treated with both acid and alkaline or both physical and chemical treatment. But the alkaline pretreatment decreases the cellulose content, this problem can be solved by controlling temperature during operation. In addition, bleaching is important in cellulose extraction because it will eliminate chromophore compound, the part of a molecule results in the color of the compound, from cellulose. Then after bleaching the color of cellulose is lighten up, which is a necessary characteristic to produce CMC [13].

2.3 Carboxymethyl cellulose from agricultural residues

Commonly, CMC is synthesized from cellulose, which contains cellulose, not less than 29 percentage of all component. The controlling quality of cellulose to be constant is necessary for the large industrial productions, which different source of raw material and different quantity will result in inconstant of cellulose properties. Using crop or agricultural residues as a precursor in the high-quality cellulose synthesis is one way to increase their value [14].

There are a lot of interesting agricultural residues in Thailand, which can be converted to valuable chemicals. Durian rind is one of them because durian is the one of the economic plant, which has high consumption both in Thailand and a foreign country. Therefore, there are a lot of wastes from durian rind, which can cause a problem in the environment. Durian rind consists of cellulose about 30 %, which is in the criteria for CMC synthesis, which require more than 29% [15]. From the study of synthesis and characterization of CMC from durian rind, the maximum DS of CMC is 0.87 with a concentration of sodium hydroxide in alkalization step is 30% w/v [16].

There is other agricultural residues used for CMC synthesis. Table 2.1 shown the different conditions in carboxymethyl cellulose synthesis with various agricultural residues. Golbaghi, L, and Khamforoush, M. [17] experimented, modeled, and optimized the carboxymethyl cellulose production from sugarcane bagasse with steam explosion pulping, the maximum DS of 1.085 was obtained at the optimum condition in CMC synthesis from sugarcane bagasse. Sugarcane bagasse consists of 23% of lignin, 19% of hemicellulose, and 40% of cellulose, which suitable for CMC synthesis [17].

The spread of water hyacinth is one of the major and continuing problems in Thailand because it is fast growing and obstruct water traffic. To decrease the amount of water hyacinth in Thailand, the CMC synthesis from water hyacinth was studied. Although the cellulose content in the water hyacinth of 24%[18] is less than the criteria for CMC synthesis but its DS is quite high about 1.67 with the optimum condition [19].

Table 2.1 Comparison of the condition in CMC synthesis from agricultural residues

Type of Agricultural residues	Initial cellulose (g)	Amount of NaOH (ml, %w/v)	Amount of MCA (g)	Time (h)	%Yield CMC	DS	Ref.
Pineapple	5	50, 40	13	6	55.58	0.50	[4]
Durian rind	15	50, 30	18	3..5	166.0	0.87	[16]
Water hyacinth	5.2	-, 10	6.2	-	149.0	1.67	[19]
Cashew tree	5	8.3, 40	2.62	3	40.00	0.90	[20]
Cotton ginning	5	30, 20	5	3	143.7	0.87	[21]
Pistachio shell	5	10, 25	6	3	-	0.82	[22]
Seaweed	10	16.67, 30	15	3	-	0.51	[23]

Note: MCA is monochloroacetic acid
CMC is Carboxymethyl cellulose

2.4 Carboxymethyl cellulose synthesis

CMC is synthesized through the carboxymethylation reaction, which is performed by two-step: alkalization and carboxymethylation reaction.

Alkalization reaction converts cellulose to alkali cellulose in the presence of sodium hydroxide (NaOH) and solvent, which is usually primary or secondary alcohol. The reaction is as shown in equation 2.1. In this step, if lignin from the cellulose extraction still remains, it will react with NaOH and decrease NaOH concentration for alkalization.

$$[C_6H_7O_2(OH)_3]_n + NaOH \rightarrow [C_6H_7O_2(OH)_2ONa]_n + nH_2O \qquad (2.1)$$

Carboxymethylation reaction is shown in the equation 2.2 and Sodium chloride (NaCl) is a by-product. Moreover, an excess amount of NaOH from the previous step lead to sodium chloroacetate and sodium glycolate formation due to NaOH may react with the monochloroacetic acid (MCA) and chloroacetate following the equation 2.3 and 2.4, respectively [24].

$$[C_6H_7O_2(OH)_2ONa]_n + nClCH_2COOH \rightarrow [C_6H_7O_2(OH)_2OCH_2COOH]_n + NaCl \qquad (2.2)$$

$$ClCH_2COOH + NaOH \rightarrow ClCH_2COONa + H_2O \qquad (2.3)$$

$$ClCH_2COONa + NaOH \rightarrow HOCH_2COONa + NaCl \qquad (2.4)$$

2.4.1 Mechanism of carboxymethylation reaction

Carboxymethylation reaction based on Williamson synthesis, which is an etherification (ether synthesis), the monochloroacetic acid ($ClCH_2COOH$, MCA) is attacked with cellulose alkoxide through an S_2N reaction. S_2N or substitution nucleophilic bimolecular is a reaction between the bonding of nucleophile (electron donor and rich electron) and a carbon atom and the breaking of halide ion in alkyl halide occur at the same time. Mechanism of S_2N is the nucleophile, cellulose alkoxide ($C_6H_7O_2(OH)_2O^-$), replace the halide ion of alkyl halide, monochloroacetic acid. Then the halide ion, chloride ion, is removed from the monochloroacetic acid and it is called a leaving group following the figure 2.5.

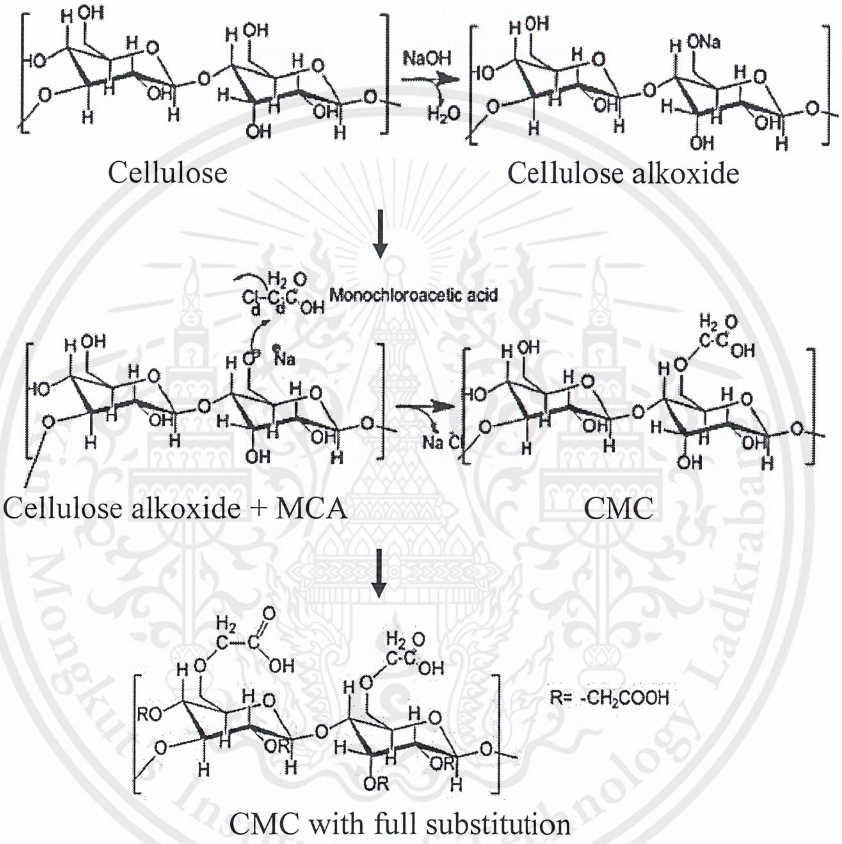


Figure 2.5 Carboxymethylation of cellulose [5].

2.4.2 Effects of the reactants mole ratio on the water solubility of CMC

Water solubility of the CMC depends on their degree of substitution (DS), which is a key property for many applications. The alkali agent (NaOH) and etherification agent (monochloroacetic acid, $ClCH_2COOH$) are important factors affect the water solubility of the CMC. The reactants mole ratios of 4:2.5:1 and 4.6:2.8:1 are the optimum compositions at 75 ºC for 1.5 h during resulting in 88-95 wt% water solubility and DS of CMCs equal 0.5-1. But the high amount of alkali affects a color of CMC become yellow due to the degradation at an excessive dosage of NaOH. Thus a too high dosage of alkali agent is not recommended and high amount of $ClCH_2COOH$ reduced the solubility of the CMC because the presence of excess acid would decrease OH^- of alkali cellulose affects alkalization of cellulose decreases too due to the nucleophile replacement in monochloroacetic acid decrease [24].

2.4.3 Effects of the solvent on the degree of substitution (DS) of CMC

The differences in polarities and stereochemistry of each solvent effect to the carboxymethylation reaction efficiency. When the polarity of the solvent decrease, the efficiency of reaction will increase. Togrul, H. and Arslan, N. [25] studied the effect of various solvents on DS when used isopropyl alcohol as medium resulted in a maximum DS of 0.558. The solvent in the carboxymethylation reaction effect to the etherifying reagent miscible with cellulose rather than form the glycolate, which is by-product [25].

2.4.4 Effects of the ratio of water and isopropyl alcohol on the degree of substitution (DS) of CMC

Pushpamalar, V., and Langford, S.J. [22] studied the effect of the ratio of water and isopropyl alcohol on DS, a maximum of 0.585 was obtained with 0:100 water: isopropyl alcohol. Furthermore, when the increase in the ratio of organic solvent, the DS of the CMC will increase. The isopropyl alcohol causes decrystallization and a change of polymorphism of cellulose. The change of crystallinity and polymorphism may be due to the partition of sodium hydroxide between the medium and the cellulose chain. This partition occurs when suspending cellulose in mixtures of an organic solvent, water, and sodium hydroxide. In such a system, the organic medium plays the role of uniformly distributing NaOH with water in cellulose and so form an 'aqueous' solution of NaOH in the cellulose phase. Isopropyl alcohol having low dielectric constant, which is a bad solvent for sodium hydroxide and it favors the higher concentration of NaOH in the vicinity of cellulose, giving rise to a substantial change of polymorphism of cellulose during alkalization [22].

2.5 Applications of carboxymethyl cellulose

There are different grades of CMC for use in industries. They are categorized by the content of CMC (%) and content of salts (%). For the application in detergents, mining flotation, technical grade, the content of CMC is less than 75% and content of salts is more than 25%. Semi-purified grade for the application in oil and gas drilling muds, the content of CMC is 75–85% and content of salts is 15–25%. Purified for the application in paper coating, textile sizing and printing, ceramic glazing, oil drilling muds, content of CMC is more than 98% and content of salts is less than 2% Extra purified)cellulose gum(Food, toothpaste, pharmaceuticals, content of CMC is more than 99.5% and content of salts is less than 0.5% [26].

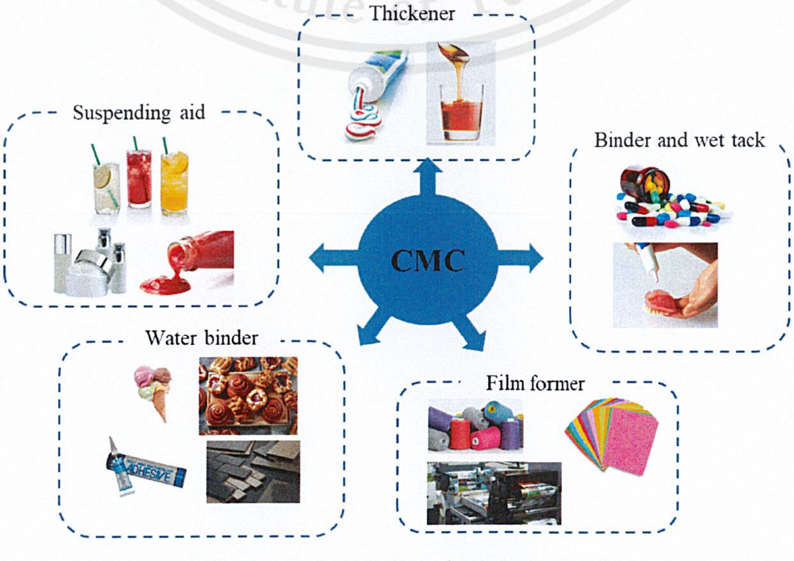


Figure 2.6 Applications of CMC

CHAPTER III
RESEARCH METHODOLOGY

3.1 Extraction of cellulose

3.1.1 Equipment

1) Erlenmeyer flask 250 ml
2) Analytical Scale 4 digits
3) Hotplate-Stirrer
4) pH meter

3.1.2 Chemicals

1) 0.5 M Hydrochloric acid (HCl)
2) 1 M Sodium hydroxide ($NaOH$)
3) 1.5% Calcium hypochlorite ($Ca(ClO)_2$)
4) Glacial acetic acid (CH_3COOH)
5) Distilled Water

3.1.3 Conditions

1) Acid-base treatment with 5%v/v H_2SO_4 and 15%w/v
2) Base treatment with 15%w/v

3.1.4 Procedure

1) 20 g of durian rind was dried at 105 ºC for 24 h.
2) Added sulfuric acid in 200 ml to the durian rind with ratio 10: 1 (liquid: solid) and stir the mixture at 70 ºC for 1 h.
3) Neutralized the sample with distilled water by vacuum filter.
4) Added 15% w/v sodium hydroxide to the sample with ratio 10: 1 (solvent: sample) and stirred the mixture at 70 ºC for 2 h.
5) Neutralized the sample with distilled water by vacuum filter.
6) Bleached with 2 g calcium hypochlorite and 1 ml glacial acetic acid for 4 h.
7) Filtered the sample and washed several times with distilled water until pH equal 7.
8) Dried the sample at 70 ºC for 12 h.
9) Grounded the sample into the powder.
10) For base treatment method is same the all above step without 2)and 3) step

3.2 Components analysis using Klason lignin

3.2.1 Equipment

1) Beaker 100 ml
2) Analytical scale 4 digits
3) Hotplate stirrer
4) Bath sonicator
5) Autoclave
6) Oven
7) Vacuum filter set
8) Filter paper 10-13 µm
9) 2 ml Pipette
10) 100 ml graduated cylinder
11) 100 ml volumetric flask
12) Heat resistant bottles

3.2.2 Chemicals

1) 98%w/w H_2SO_4
2) Distilled water
3) Durian rind

3.2.3 Procedure

1) Weigh 0.2 g durian rind and place it into the bottle. Then, dried the sample at 105 ºC for 4 hr to make sure that no moisture in the sample.
2) After dried for 4 hr, removed the sample from the oven and closed it with cover. Then, kept the sample in the silica gel box to cool down.
3) Prepared 72%wt H_2SO_4 solution from 66 ml of 98%wt H_2SO_4 in 100 ml volumetric flask and added distilled water to 100 ml.
4) Put the sample from 2) into 100 ml beaker and added 2 ml of 72%wt H_2SO_4 solution. Then, place it into the sonicator shaken for 2 min and removed from sonicator for 2 min to cool down. Repeated these steps until complete 2 hr.
5) Diluted concentration of H_2SO_4 in the mixture to 3%wt by added 75 ml distilled water into the mixture from 4). Transferred the mixture to the heat resistance bottle and closed the lid.
6) Added the sample from 5) to the autoclave at 121 ºC for 1 hr.
7) Weigh filter paper after dried it for 1 hr at 60 ºC and recorded the weight.
8) After the sample cooled down, filtered the sample with vacuum filter. Dried the filter paper, which contained the solid particles, at 105 ºC for 24 hr. Then, weigh it to determined klason lignin component in the sample.
9) The liquid phase from filtration is analyzed by HPLC to determined content of cellulose and hemicellulose. (detail in appendix A.1)

3.3 Synthesis of CMC from agricultural residue cellulose

3.3.1 Equipment

1) Erlenmeyer flask 600 ml
2) Analytical Scale 4 digits
3) Hotplate stirrer
4) Vacuum filter set
5) Filter paper 10-13 µm
6) pH meter

3.3.2 Chemicals

1) Isopropyl alcohol
2) 30%w/v Sodium hydroxide (NaOH)
3) Monomonochloroacetic acid (MCA, $ClCH_2COOH$)
4) Acetic acid 1 M
5) Absolute methanol in commercial grade

3.3.3 Conditions

This work studied the condition as shown in table 3.1

Table 3.1 Reaction Conditions

Parameter	**Condition**
Reactants mole ratio (mol NaOH: mol $ClCH_2COOH$)	1:1, 2:1, 4:1, 1:2
Time for Carboxymethylation (h)	3, 6

3.3.4 Procedure

Alkalization:

Mixed 5 g of agricultural waste cellulose with 300 ml mixture of isopropyl alcohol-water (volume ratio, 4: 1) and 40 ml of various concentration (10, 20 and 30 %w/v NaOH) of NaOH solution and stirred for 2 h.

Carboxymethylation:

1) Added varying amount of monochloroacetic acid (5, 8, 9.45 and 20 g) and stirred the alkali cellulose at 55 ºC and continuously stirred the mixture for varying time in carboxymethylation (3,6 h).
2) The mixture is separated in 2 phases, suspended the solid phase with 100 ml methanol for 40 min.
3) Adjusted pH of the slurry to 7 with 1 M acetic acid.
4) Filtered and washed with 400-500 ml absolute methanol to remove excess reagent and salt.
5) CMC was dried at 60 ºC for 12 hr.
6) Analyze the obtained CMC by Fourier- transform infrared spectroscopy (FT-IR).
7) Determined the degree of substitution (DS) follow the ASTM D1439

3.4 Determination of the degree of substitution (DS)

The degree of substitution of obtained CMC was investigated according to ASTM D1439: a standard test method for sodium carboxymethylcellulose.

3.4.1 Equipment

1) Beaker 250 ml
2) Erlenmeyer flask 250 ml
3) Analytical Scale 4 digits
4) Vacuum filter set
5) Filter paper 10-13 μm
6) pH meter
7) Stirring rod
8) Burette
9) Clamp and stand

3.4.2 Chemicals

1) 70%vol methanol
2) 65%wt nitric acid (HNO_3)
3) 95%vol ethanol
4) 0.5 M NaOH solution
5) 0.3 M HCl solution
6) Distilled water

3.4.3 Procedure

1) Mixed 1 g CMC with 50 ml of 95%vol ethanol in 250 ml beaker and stirred. Then, added 5 ml of 2 M HNO_3 and stirred for 10 min at room temperature
2) Heated the mixture to boiling for 5 min and stirred further for 20 min without heat and left to settle.
3) The mixture was filtered and washed with 95%vol ethanol to remove surplus acid and salt.
4) The mixture was washed with methanol and transferred to beaker and heated until the alcohol was removed. Dried the sample in the oven at 90 °C for 3 hr.
5) 0.5 g dried sample was dissolved in 100 ml distilled water and 25 ml of 0.5 M NaOH mixture.
6) Titrate the mixture from step 4) with 0.3 M HCl.
7) Calculated the DS value followed equation (3.1) and (3.2)

$$DS = \frac{0.162A}{(1 - 0.058A)} \tag{3.1}$$

$$A = \frac{(BC\text{-}DE)}{F} \tag{3.2}$$

Where

A is the equivalent weight of alkali required per gram sample
B is the amount of NaOH solution (ml)
C is the concentration of NaOH solution (molarity)
D is the amount of HCl solution (ml)
E is the concentration of HCl solution (molarity)
F is the weight of the sample (g)

3.5 Characterization of CMC

FT-IR was used to verify the characteristic of CMC by observing the spectra Each spectra (band) from FT-IR indicate the functional group or structure of organic compounds. The important band that indicates the presence of CMC consist of band ~1060 cm^{-1} represents $CH\text{-}O\text{-}CH_2$ stretching, the band ~1450 cm^{-1} correspond to $-CH_2$ scissoring, the band ~1600 cm^{-1} correspond to C=O stretching and the band 3200-3600 cm^{-1} correspond to O-H stretching.

The hydrolysis of CMC to glucose is another one method to characterize the presence of CMC by calculating the obtained glucose content from CMC back to the CMC content. But this method will be studied to verify that it can indicate the presence of CMC.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Cellulose extraction from durian rind

This study compared two methods of cellulose extraction from durian rind, the acid-base treatment, and base treatment. The aim is to eliminate lignin from the lignocellulose structure. Table 4.1 shows the lignin content before and after extraction. The raw material, durian rind, contained 22.03 %wt lignin. When extracted the cellulose from the durian rind using acid-base treatment method, the remaining lignin content equals to 13.76% and 11.04% from 2 runs of same condition of 200 ml of 5%v/v H_2SO_4 at 70 °C for 1 h and 200 ml of 15%w/v NaOH at 70 °C for 2 h. The remaining lignin content after extracted using base treatment method equals to 8.47% and 9.02% from 2 runs of the same condition of 200 ml of 15%w/v NaOH at 70 °C for 2 h. The base treatment method can remove more lignin content than the acid-base treatment due to the concentration of sodium hydroxide in the base step of acid-base treatment decreased might due to the remaining sulfuric acid after the neutralization after acid step reacts with sodium hydroxide in the base step. This affects the efficiency of lignin removal of sodium hydroxide in this step will be decrease. On the other hand, the yield of cellulose from both extraction methods are similar because the concentration of acid and base, which used in the experiment does not affect the cellulose content.

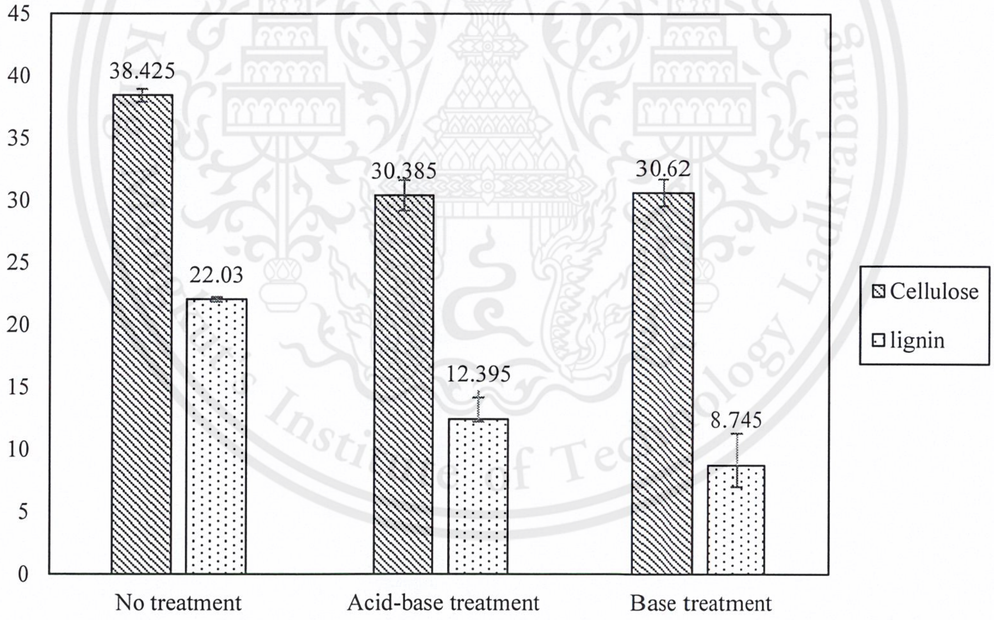


Figure 4.1 Comparison of cellulose extraction method

4.2 Synthesis of carboxymethyl cellulose

4.2.1 Characterization of CMC

The FT-IR spectra of cellulose from durian rind, CMC from durian rind and CMC from commercial cellulose powder is shown in figure 4.2. The cellulose and CMC from durian rind had the same band except for the band at 1600 cm^{-1} due to C=O stretching. This band of CMC is sharper than cellulose because of the presence of substitution of carboxymethyl group. From the comparison of FT-IR spectra of CMC from durian and commercial cellulose powder, the band at 1600 cm^{-1} due to C=O stretching of CMC from commercial cellulose powder is sharper than the CMC from durian rind because the lignin content in CMC from commercial cellulose powder is less than in the CMC from durian rind. The remaining lignin will react with the NaOH in alkalization resulting in a decrease in concentration of NaOH to react with cellulose. This affects the substitution of carboxymethyl group is decreased.

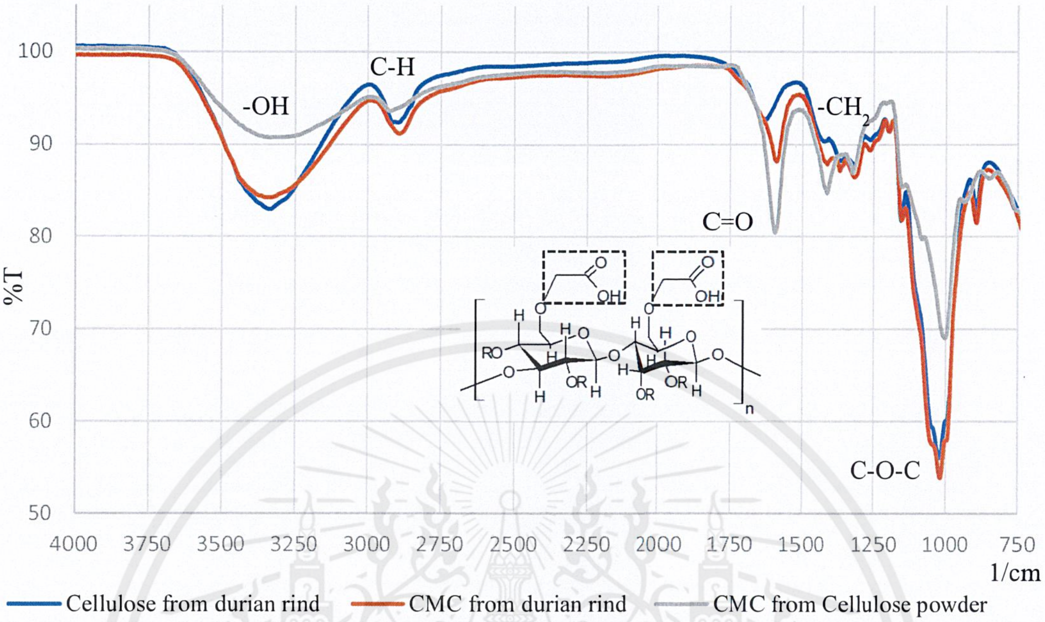


Figure 4.2 Overlay FT-IR spectras of cellulose from durian rind, CMC from durian rind and CMC from cellulose powder

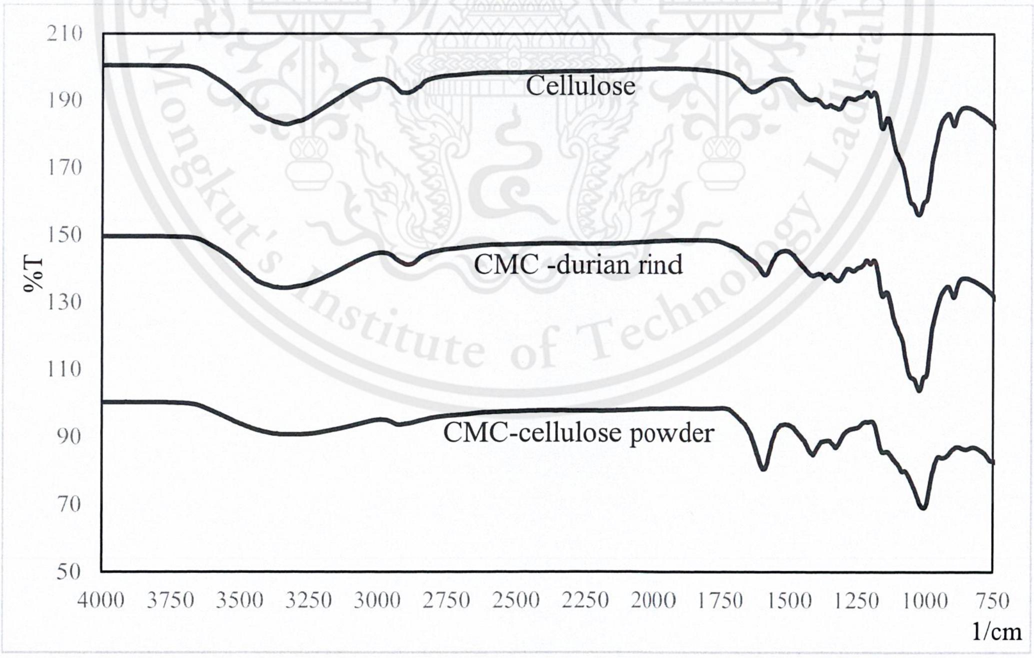


Figure 4.3 FT-IR spectras of cellulose from durian rind, CMC from durian rind and CMC from cellulose powder

4.2.2 Effect of reactant ratio to the degree of substitution (DS)

The CMC synthesis consists of 2 step, alkalization, and carboxymethylation. Alkalization is the reaction between cellulose and NaOH convert to alkali cellulose at room temperature. Carboxymethylation is the reaction between monochloroacetic acid (MCA, $ClCH_2COOH$) and alkali cellulose at 55 °C and converts to carboxymethyl cellulose.

Table 4.2 shows the effect of mole ratio between NaOH and MCA to DS value of CMC. The reactant ratio of 1:1 resulted in a maximum DS of 1.11. When DS decrease with increasing of NaOH because excess NaOH concentration affects to glycolate, which is by-product, formation. But the DS decreases when a mole of MCA increase because the active sites on alkali cellulose is available to substitution of carboxymethyl group.

To compare the DS of obtained CMC from durian rind of our study (experimental No.5) and previously studied of Rachtanapun et al. [16], at the same reactants ratio. Our DS is 1.05 and Rachtanapun et al. obtained DS of 0.87. The DS is not equal because of the initial amount of cellulose for the reaction was not equal. This might be the effect of the ratio of solvent to the initial amount of cellulose. Our ratio of solvent to cellulose is 300 ml to 5 g and Rachtanapun is 300 ml to 15 g. The lower initial amount of cellulose is complete miscible and the reactant is more accessible to react.

Table 4.1 Degree of substitution of CMC with different reactant ratio

No.	**Reactants mole ratio (mol NaOH: mol MCA)**	**Degree of substitution**
1	1:1	1.11
2	2:1 (0.2:0.085)	1.03
3	4:1	0.43
4	1:2	0.47
5	2:1 (0.375:0.19)	1.05

4.2.3 Effect of time in carboxymethylation step to the degree of substitution (DS)

Table 4.2 shows an increase in the DS with increasing reaction time for the reactant ratio 4:1 due to the fact that there is better reaction environment created and a longer time available for carboxymethylation. Prolonging the duration of the reaction results in the favorable effect of time on absorption of the reactants with affects to the contacts between the etherifying agent, which is sodium hydroxide and monochloroacetic acid, and cellulose is increase following the figure 4.4. For the reactant ratio 1:1, the DS decrease when the reaction time increase. Because the reaction with ratio 1:1 has no more active site for carboxymethylation after 3 hours. The lower DS after 3 hours might cause by the bond breaking at β-(1-4) glycosidic bond by sodium hydroxide in the solution, which can be illustrated by figure 4.5.

Table 4.2 Degree of substitution of CMC with a different time in carboxymethylation

No.	Reactants mole ratio (mol NaOH: mol MCA)	Time in carboxymethylation step (hr.)	Degree of substitution
3	4:1	3	0.43
5		6	1.11
1	1:1	3	1.11
6		6	0.7

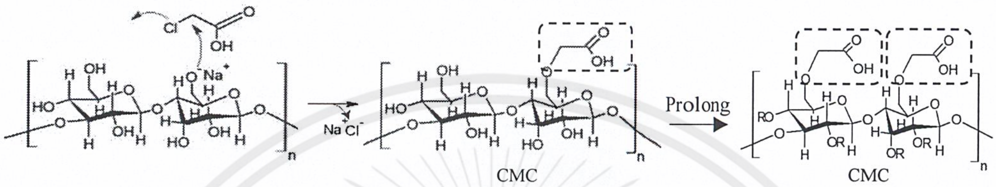


Figure 4.4 Carboxymethylation reaction after 6 h.

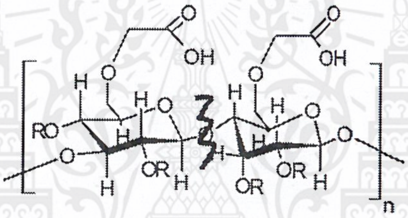


Figure 4.5 The breaking of β-(1-4) glycosidic bond

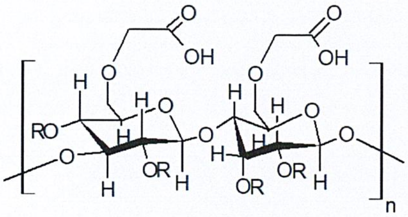
4.2.4 Calculation of the theoretical degree of substitution (DS)

Idealized possible unit structure of carboxymethyl cellulose (CMC) with a DS of 1.0 with the substitution hydroxyl group 1 position on 1 molecule anhydrous glucose with carboxymethyl group. The substitution of carboxymethyl group 1 molecule obtained from the bonding between 1 molecule sodium hydroxide with 1 molecule of anhydrous glucose. This assumption can be verified from equation 4.1 and 4.2. The equation 4.1 show that 1 mol OH^- of NaOH react with 1 mol H^+ of anhydrous glucose. The equation 4.2 show that 1 mol Cl^- of monochloroacetic acid (MCA) react with 1 mol Na^+ of alkali cellulose. We can summarized that the reactants ratio in CMC synthesis is 1:1:1 (mol glucose: mol NaOH: mol MCA).

$$[C_6H_7O_2(OH)_3]_n + NaOH \rightarrow [C_6H_7O_2(OH)_2ONa]_n + nH_2O \qquad (4.1)$$

$$[C_6H_7O_2(OH)_2ONa]_n + ClCH_2COOH \rightarrow [C_6H_7O_2(OH)_2OCH_2COOH]_n + NaCl \qquad (4.2)$$

The DS would be 3.0 if all three hydroxyl groups, which is represented in “R” in figure 4.6, on anhydrous glucose unit were substituted. A DS of 3.0 is the theoretical maximum for CMC.



R: $-CH_2COOH$

Figure 4.6 Full substitution of Carboxymethyl cellulose.

4.2.5 The solubility of CMC from durian rind and cellulose powder compared with cellulose powder

To compare the solubility of CMC and cellulose, 0.1 of CMC from durian rind, CMC from cellulose powder and cellulose powder is mixed with 50 ml of distilled water. From the figure 4.6 found that some part of the cellulose powder remained after dissolved with distilled water compared to CMC from durian rind cellulose and CMC from cellulose powder.


Cellulose powder

CMC from durian rind

CMC
from Cellulose powder

Figure 4.7 The solubility of cellulose powder, CMC from durian rind and CMC from cellulose powder

CHAPTER V
CONCLUSIONS

5.1 Summary of the results

The senior project studied optimized the condition for cellulose extraction and CMC synthesis using durian rind. The results can be summarized as follows:

From the results, the base treatment with condition 15%w/v NaOH at 70°C for 2 hours is appropriate method for cellulose extraction. The remaining lignin content from base treatment is 8.74, which less than the acid-base treatment.

The appropriate conditions to the synthesis of CMC using durian rind was the reactant ratio 1:1 for 3 hours to obtained CMC with the DS of 1.11. A decrease in DS with the increasing of monochloroacetic acid. The DS increase with the time carboxymethylation. For the reactant ration 1:1 the DS decrease when the time carboxymethylation higher than 3 hours.

5.2 Suggestions

5.2.1 Other substrates might be studied in addition to durian rinds such as banana peel, orange peel or groundnut shell.

5.2.2 The analysis of the results, the sodium chloride content in CMC should be studied for the synthesis of food grade carboxymethyl cellulose.

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APPENDIX

APPENDIX A
SAMPLE OF CALCULATION

A.1 Calculation of klason lignin

The lignin content in the substrate determined from the solid part from klason lignin.

$$\%\text{lignin} = \frac{\text{Mass of klason lignin}}{\text{Mass of substrate}} \times 100 \qquad \text{(A.1)}$$

Example: To calculated the lignin content in durian rind 0.20050 g

Weight of filter paper + foil = 1.47770 g

Weight of filter paper + foil + klason lignin after dried = 1.52225 g

klason lignin = 0.04455 g

$$\%\text{lignin} = \frac{0.04455}{0.20050} \times 100$$

$$= 22.22\ \%$$

Table A.1 Lignin content in the durian rind before and after extraction

No.	**Lignin content (%)**		
	Before extraction	**After acid-base treatment**	**After base treatment**
1	22.22	14.15	5.10
2	21.84	13.36	11.84
3	-	12.53	10.22
4	-	9.54	7.82

A.2 Calculation the yield of cellulose

Calculation of cellulose in substrate 0.2 g obtained from injection of the liquid part from klason lignin into the HPLC to determined cellulose and xylose content and converted to the cellulose and hemicellulose content.

$$\%\text{yield cellulose} = \frac{\text{Mass of cellulose}}{\text{Mass of initial durian rind}} \times 100 \qquad \text{(A.2)}$$

Table A.2 Peak area of the liquid phase from klason lignin after HPLC analysis

Substrate	**Peak area (mV.s)**	
	No. 1	No. 2
Durian rind	70.803	72.725

Determined the concentration of glucose from calibration curve between the concentration of glucose and peak area follow figure A.1.

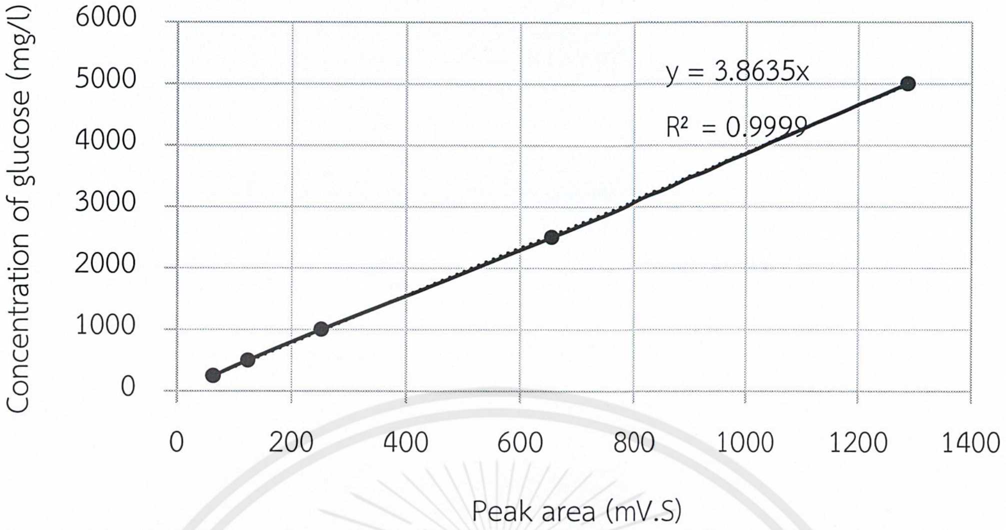

Figure A.1 Calibration curve of glucose concentration (ppm)

Multiply the concentration of glucose(mg/l) by 4 due to the dilution sample before HPLC analysis. And multiply by volume of substrate and conversion factor (77)/(1,000 (ml/l) x 1000 (g/mg)) obtained mass of glucose. Then, determined yield of glucose from divided the mass of glucose by mass of substrate and multiply by 100 and converted yield of glucose to yield of cellulose by multiply by 0.9 (When glucose molecule bonded, molecule of water will release; (180-18)/180 = 0.9).

$$\text{Mass of glucose} = \frac{\text{Concentration of glucose } \left(\frac{\text{mg}}{\text{l}}\right) \times \text{ volume of substrate (ml)}}{1000(\text{ml/l}) \times 1000\ (\text{g/mg})} \qquad \text{(A.3)}$$

Example: Calculation of cellulose content in durian rind 0.2005 g

Concentration of glucose obtained curve = (3.8635 x Peak area) = 3.8635 x 70.803

= 273.547 mg/l

Dilute the sample before HPLC analysis by add water 6 ml;

Concentration of glucose = 273.547 x 4 = 1094.188 mg/l

$$\text{Mass of glucose} = \frac{1094.188\ (\text{mg/l}) \times 77\ (\text{ml})}{1000(\text{ml}) \times 1000\ (\text{mg})} = 0.08425$$

$$\text{\%yield glucose} = \frac{0.08425}{0.2005} \times 100 = 42.02$$

%yield cellulose = 0.9 x 42.02 = 37.82 %

A.3 Calculation of Degree of substitution (DS)

Degree of substitution (DS) of CMC calucated followed equation A.3 and A.4.

$$\mathrm{DS} = \frac{0.162 \times A}{(1 - 0.058A)} \tag{A.3}$$

$$A = \frac{(BC - DE)}{F} \tag{A.4}$$

Where

A is the equivalent weight of alkali required per gram sample
B is the amount of NaOH solution (ml)
C is the concentration of NaOH solution (molarity)
D is the amount of HCl solution (ml)
E is the concentration of HCl solution (molarity)
F is the weight of the sample (g)

This work used 25 ml (B) of 0.5 M (C) NaOH mixed with the CMC and 0.3 M (E) HCL with volume follow table A.3.

Table A.3 Results of the calculation of the DS

CMC No.	mol NaOH: mol MCA	Volume HCL (ml)	A	DS
1	0.275: 0.21 (1:1)	33.5	4.9	1.11
2	0.2: 0.085 (2:1)	33.9	4.66	1.03
3	0.2: 0.053 (4:1)	37.8	2.32	0.43
4	0.15: 0.3 (1:2)	37.5	2.5	0.47
5	0.2: 0.053, 6 hr (4:1)	33.5	4.9	1.11
6	0.1: 0.1, 6h (1:1)	35.9	3.46	0.70
7	0.1: 0.1 (1:1)	33.8	4.72	1.05
8	0.375: 0.19 (2:1)	33.8	4.72	1.05

Example: To calculated the DS of CMC with reactant ratio= 0.2: 0.053
Weight of CMC used 0.5 g;

$$A = \frac{(25\times0.5) - (37.8\times0.3)}{0.5} = 2.32$$

$$\mathrm{DS} = \frac{0.162 \times 2.32}{1 - (0.058\times2.32)} = 0.43$$

APPENDIX B

ASTM D1439: STANDARD TEST METHODS FOR SODIUM CARBOXYMETHYLCELLULOSE

The degree of substitution of obtained CMC was investigated according to ASTM D1439: a standard test method for sodium carboxymethylcellulose.

B.1 DEGREE OF ETHERIFICATION

Scope

1. These test methods cover the determination of the degree of etherification)D.E.(of sodium carboxymethyl cellulose.
2. Two test methods are included as follows:
   - 2.1 Test Method A)Acid Wash(, for crude grades of sodium carboxymethyl cellulose with degrees of etherification up to 0.85. Above 0.85 degree of etherification, slightly low results may be obtained.
   - 2.2 Test Method B)Nonaqueous Titration(, for purified grades of sodium carboxymethyl cellulose of all degrees of etherification. It is not applicable to the crude grades.

1. Test Method A)Acid Wash(

Summary of Test Method: The water-soluble sodium carboxymethylcellulose is converted to the insoluble acid form, purified by washing, dried, and then a weighed sample is reconverted to the sodium salt with a measured excess of sodium hydroxide.

Significance and Use: These test methods determine the amount of substituent groups added to the cellulose backbone. The level can greatly affect solution properties, rheology, viscosity, hygroscopicity, salt tolerance, and many other properties of the polymer.

1.1 Apparatus

1.1.1 Stirrer, air-driven.

1.1.2 Buchner Funnel, 75-mm, fitted with a 70-mm finetexture, heavy-duty filter paper. A 60-mm medium-porosity, fritted glass funnel may also be used.

1.1.3 Drying Oven, maintained at 105°C.

1.2. Reagents

1.2.1 Diphenylamine Reagent—Dissolve 0.5 g of diphenylamine in 120 mL of sulfuric acid)H2SO4, 9 + 2(. The reagent should be essentially water-white. It will give a deep blue coloration with traces of nitrate or other oxidizing agents.

1.2.2 Ethyl Alcohol)95 volume %(—Denatured ethyl alcohol conforming to either Formula 2B, 3A, or 30 of the U. S. Bureau of Internal Revenue.

1.2.3 Ethyl Alcohol)80 % by volume(—Dilute 840 mL of Formula 2B, 3A, or 30 denatured alcohol to 1 L with water.

1.2.4 Hydrochloric Acid, Standard)HCl, 0.3 to 0.5 N(.

1.2.5 Methanol, anhydrous.

1.2.6 Nitric Acid)sp gr 1.42(—Concentrated nitric acid)HNO_3(.

1.2.7 Sodium Hydroxide, Standard Solution)0.3 to 0.5 N(— Prepare and standardize a 0.3 to 0.5 N solution of sodium hydroxide)NaOH(.

1.2.8 Sulfuric Acid)9 + 2(—Carefully mix 9 volumes H_2SO_4 with 2 volumes of water.

1.3 Procedure

1.3.1 Weigh approximately 4 g of the sample into a 250-mL beaker and add 75 mL of ethyl alcohol)95 %(. Stir the mixture with an air–driven stirrer until a good slurry is obtained.

1.3.2 Add 5 mL of HNO3, while agitating, and continue agitation for 1 to 2 min. Heat the slurry and boil for 5 min.)Warning—Exercise care to avoid fire.(Remove the heat and continue agitation for10 to 15 min.

1.3.3 Decant the supernatant liquid through the filter and transfer the precipitate to the filter with 50 to 100 mL of ethyl alcohol)95 %(. Wash the precipitate with ethyl alcohol)80 %(that has been heated to 60°C, until all of the acid has been removed.

1.3.4 Test for the removal of acid and salts)ash(by mixing a drop of the acid carboxymethylcellulose slurry from the filter with a drop of diphenylamine reagent on a white spot plate. A blue color indicates the presence of nitrate and the necessity for further washing. If the first drop of reagent does not produce a blue color, further drops should be added until an excess of reagent is known to be present, noting the color after each drop. Four to six washings will usually suffice to give a negative test for nitrate.

1.3.5 Finally, wash the precipitate with a small amount of anhydrous methanol and draw air through it until the alcohol is completely removed. Transfer the precipitate to a glass or aluminum weighing dish provided with a cover. Heat the uncovered dish on a steam bath until the odor of alcohol can no longer be detected)in order to avoid fires due to methanol fumes in the oven(, then dry the dish and contents, uncovered for 3 h at 105°C. Place the cover on the dish and cool to room temperature in a desiccator.

1.3.6 The sulfate ash content of the sample at this point should be less than 0.5 % when determined on 0.5 g of the sample by the procedure given in the Ash as Sulfate section of Test Methods D 1347. If the ash content is greater than 0.5 %, rewash the sample with ethyl alcohol)80 %(. If necessary, repeat the procedure described in 13.1-13.3 to 13.4.

1.3.7 Weigh, to the nearest 0.01 g, about 1 to 1.5 g of the dried acid carboxymethylcellulose)depending on the normality of the acid and base to be used(into a 500-mL Erlenmeyer flask. Add 100 mL of water and 25.00 mL of 0.3 to 0.5 N NaOH solution, while stirring. Heat the solution to boiling, and boil for 15 to 30 min.

1.3.8 Titrate the excess NaOH, while the solution is hot, with the 0.3 to 0.5 N HCl to a phenolphthalein end point.

1.4 Calculation

1.4.1 Calculate the degree of etherification, G, as follows:

$$G = \frac{0.162 \times A}{(1 - 0.058A)}$$

$$A = \frac{(BC - DE)}{F}$$

Where

A is the equivalent weight of alkali required per gram sample
B is the amount of NaOH solution (ml)
C is the concentration of NaOH solution (molarity)
D is the amount of HCl solution (ml)

E is the concentration of HCl solution (molarity)
F is the weight of the sample (g)
162 = gram molecular mass of the anhydroglucose unit of cellulose
58 = net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted.

1.5 Precision and Bias

1.5.1 Precision— Statistical analysis of interlaboratory)repeatability(test results indicates a precision of 60.04 D.E. units at the 95 % confidence level.

1.5.2 Bias—No justifiable statement can be made on the bias of the procedure for measuring the degree of etherification because no suitable reference material exists.

2.Test Method B—Nonaqueous Titration

Summary of Test Methods: This measurement is based upon a nonaqueous acid-base titration. The sample is refluxed with glacial acetic acid, and the resulting sodium acetate is titrated with a standard solution of perchloric acid in dioxane, to a potentiometric end point. Impurities containing alkaline sodium will also be titrated under these conditions. Sodium chloride does not interfere.

2.1 Apparatus

2.1.1 *pH Meter*, equipped with a standard glass electrode and a calomel electrode modified as follows:

2.1.1.1 Discard the aqueous potassium chloride solution, then rinse and fill with the calomel electrode solution

2.1.1.2 Add a few crystals of potassium chloride and silver chloride or silver oxide to the electrode.

2.2.2 *Buret*, micro, 10-mL capacity.

2.2 Reagents

2.2.1 *Acetic Acid*, glacial.

2.2.2 *Calomel Electrode Solution*—Add 2 g of potassium chloride (KCl) and 2 g of silver chloride (AgCl) or silver oxide (Ag_2O) to 100 mL of methanol and shake thoroughly to saturate. Use the supernatant liquid.

2.2.3 *1,4-Dioxane*.

2.2.4 *Perchloric Acid* (0.1 *N*)—Add 9 mL of concentrated perchloric acid ($HClO_4$, 70 % to 1 L of dioxane, with stirring (**Warning**—The solution of perchloric acid in dioxane should never be heated or allowed to evaporate.). Store in an amber glass bottle. Any slight discoloration that appears on standing may be disregarded.

2.2.4.1 Standardize the solution as follows: Dry potassium acid phthalate for 2 h at 120°C. Weigh 2.5 g to the nearest 0.0001 g into a 250-mL volumetric flask. Add glacial acetic acid, shake to dissolve, and then make up to volume and mix thoroughly.

2.2.4.2 Pipet 10 mL into a 100-mL beaker and add 50 mL of acetic acid. Place on a magnetic stirrer and insert the electrodes of the pH meter.

2.2.4.3 Add nearly the required amount of $HClO_4$ from a buret, then decrease the increments to 0.05 mL as the end point is approached. Record the millilitres of titrant versus millivolts, and continue the titration a few millilitres beyond the end point.

2.2.4.4 Plot the titration curve and read the volume of titrant at the inflection point. Calculate the normality, N, as follows:

$$N= (A \times 10 \times 1000)/(B \times 204.22 \times 250)$$

where:

A = potassium acid phthalate used, g,
B = $HClO_4$ added, mL,
204.22 = gram molecular mass of potassium acid phthalate,
10 = potassium acid phthalate solution added, mL,
250 = glacial acetic acid used to dissolve potassium acid phthalate, mL.

2.2.5 *Potassium Acid Phthalate*, primary standard, National Institute of Standards and Technology Standard Sample No. 84.

2.3 Procedure

21.1 Weigh 0.2 g of the sample, to the nearest 0.0001 g, into a 250-mL Erlenmeyer flask with the ground-glass joint. Add 75 mL of acetic acid, connect to a water-cooled condenser, and reflux gently on a hot plate for 2 h.

21.2 Cool and transfer the solution to a 250-mL beaker with the aid of 50 mL of acetic acid. Place on the magnetic stirrer and titrate to a potentiometric end point with 0.1 *N* $HClO_4$

2.4 Calculation

2.4.1 Calculate the degree of etherification, *H*, as follows (Note 1):

$$M =(AN \times 10) /(G \times(100- B))$$

$$H = 0.162\ M/(1.000 - 0.080\ M)$$

where:

M = milliequivalents of acid consumed per gram of sample,
A = HClO4 added, mL,
N = normality of $HClO_4$,
G = sample used, g,
B = percent moisture, determined on a separate sample, in accordance with Sections 4-7,
162 = gram molecular mass of an anhydroglucose unit of cellulose, 80 = net increase in molecular mass of an anhydroglucose unit for each sodium carboxymethyl group added.

NOTE 1—The result calculated in accordance with Section 18 includes the alkaline sodium from sodium glycolate; however, if the latter is less than 0.5 %, the interference is negligible.

2.5 Precision and Bias

2.5.1 *Precision*—Statistical analysis of interlaboratory test results indicates the precision of this test method as shown below:

Approximate D.E. Level	Precision, D.E. Units (95 % Confidence Level)
0.40	±0.010
0.80	±0.012
1.35	±0.038

2.5.2 *Bias*—No justifiable statement can be made on the bias of the procedure for measuring degree of etherification because no suitable reference material exists.

B.2 Determination of sodium chloride (NaCl) content

The sodium chloride (NaCl) content of obtained CMC was investigated according to ASTM D1439: a standard test method for sodium carboxymethylcellulose.

3.5.1 Equipment
1) Beaker 250 ml
2) Analytical Scale 4 digits
3) Stirring rod
4) Burette
5) Clamp and stand

3.5.2 Chemicals
1) 65%vol methanol
2) 65%wt nitric acid (HNO_3)
3) 0.015 N $AgNO_3$
4) Distilled water

3.5.3 Experimental
1) Added 0.025g sample into 10 ml of 65% methanol and kept for 5 h.
2) Neutralized the liquid phase from step 1) with dilute HNO_3
3) Titrated the mixture with 0.015 N $AgNO_3$ solution.
4) Calculated the NaCl content followed the equation (3.3)

$$\%NaCl = 0.0147 \times \frac{V}{m} \qquad (3.3)$$

Where

V is the amount of $AgNO_3$ (ml)
m is the weight of the dried sample (g)

APPENDIX C
FT-IR RESULTS OF ALL

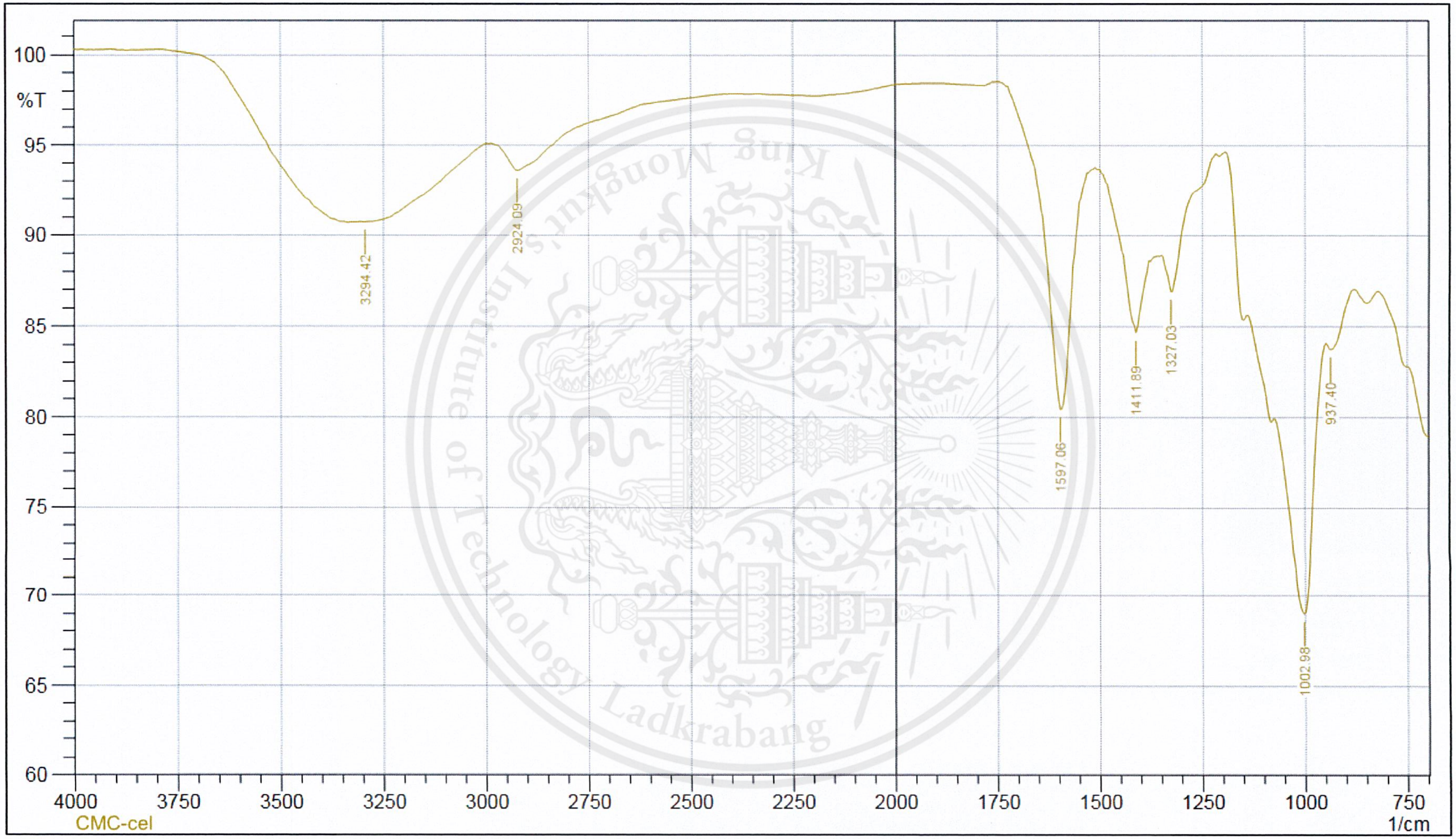

Figure C.1 FT-IR spectra of CMC from cellulose powder

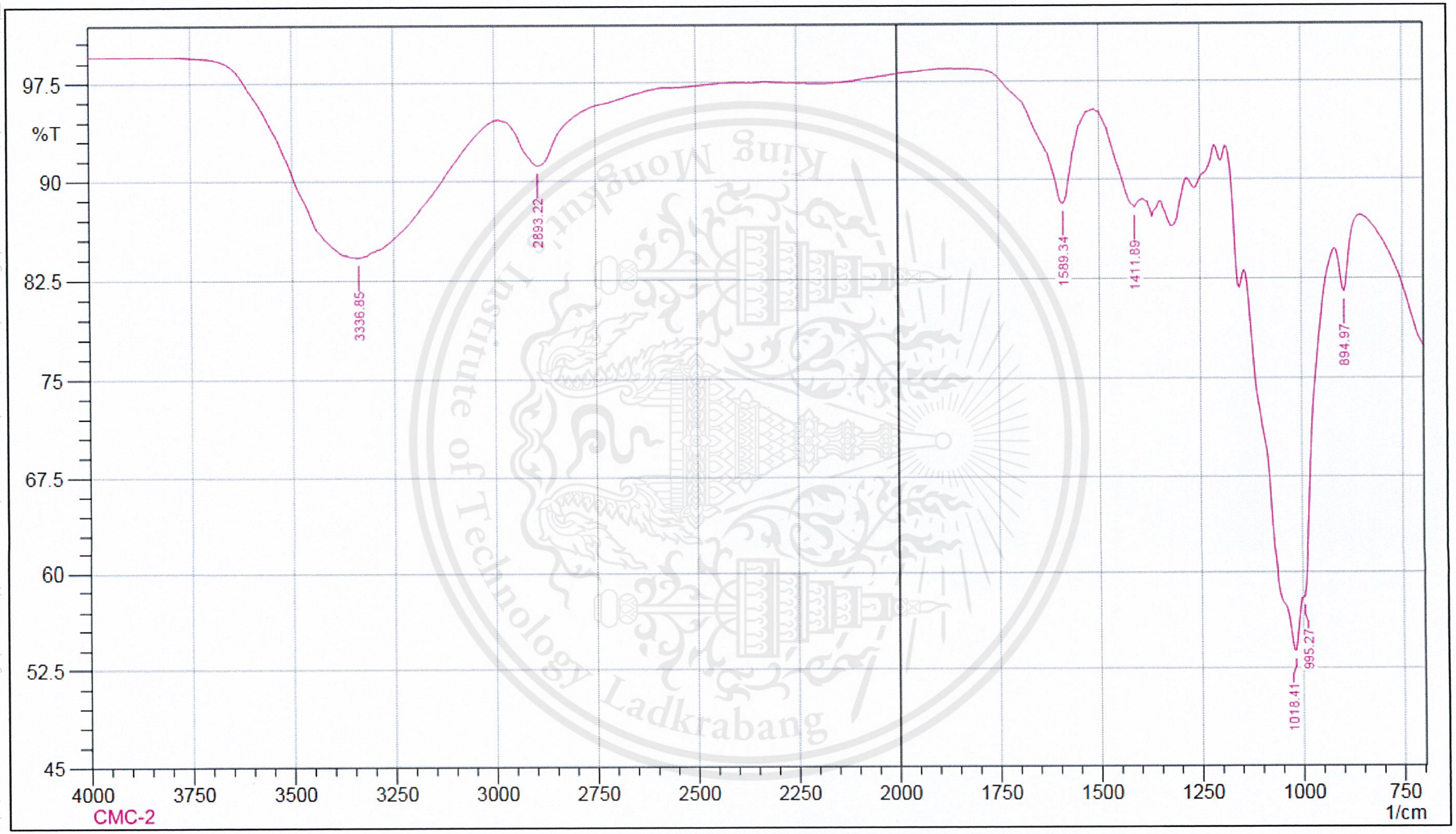

Figure C.2 FT-IR spectra of CMC from durian rind with reactant ratio 2:1

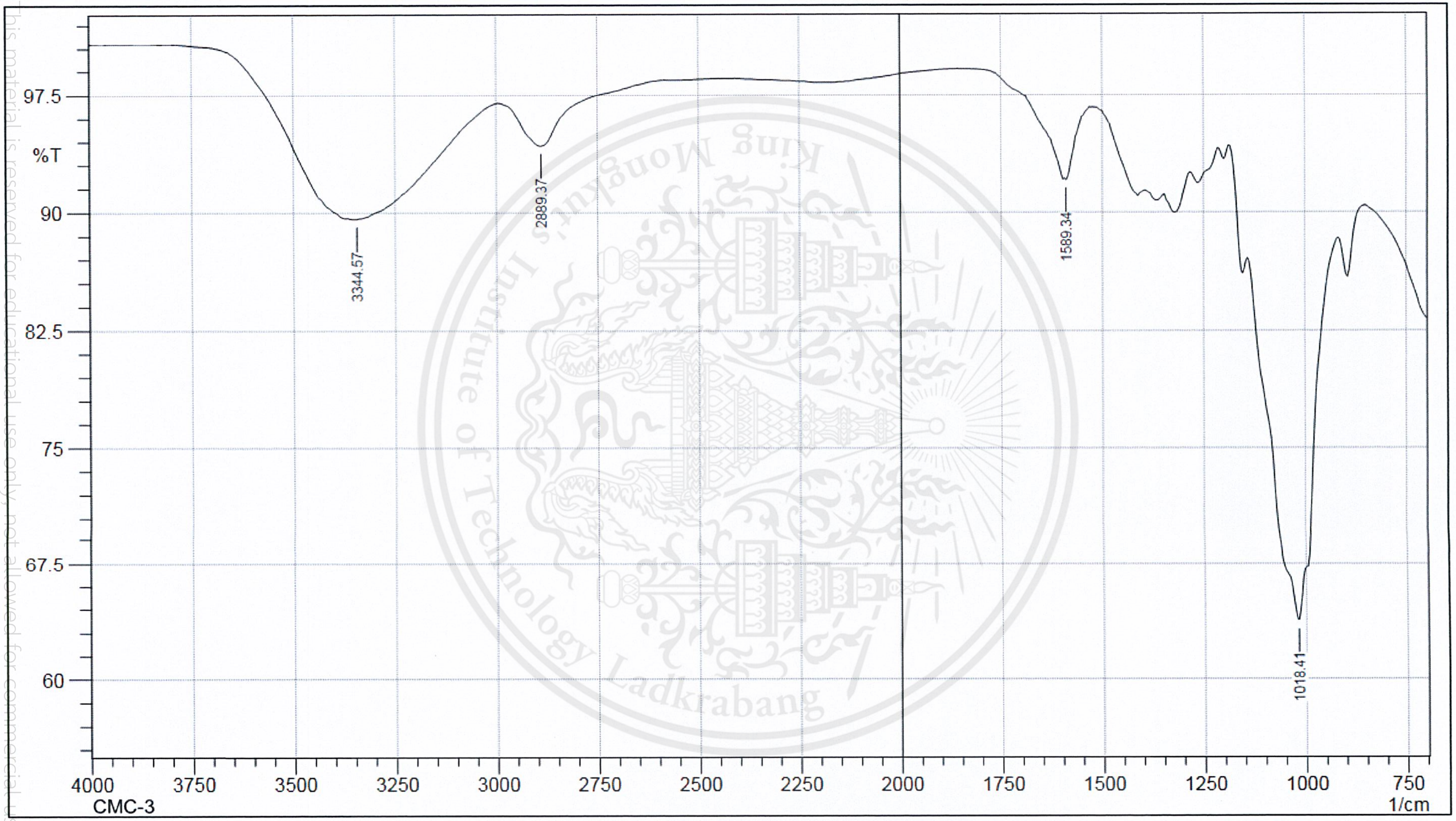

Figure C.3 FT-IR spectra of CMC from durian rind with reactant ratio 4:1

APPENDIX D
EQUIPMENT USED IN THE EXPERIMENT

Figure D.1 Durian ring chip

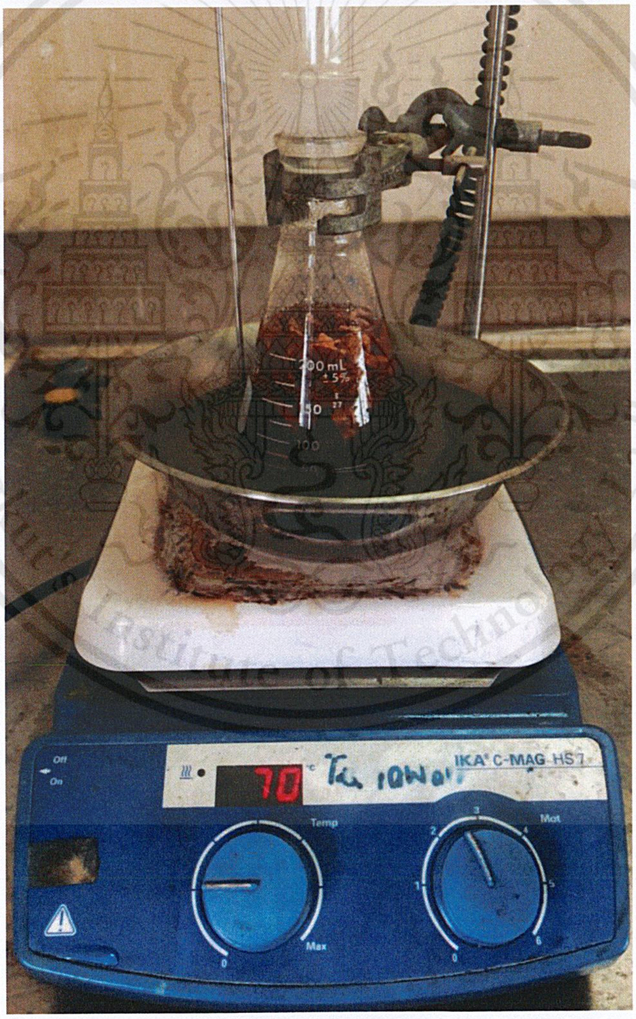

Figure D.2 Set-up the cellulose extraction from durian rind

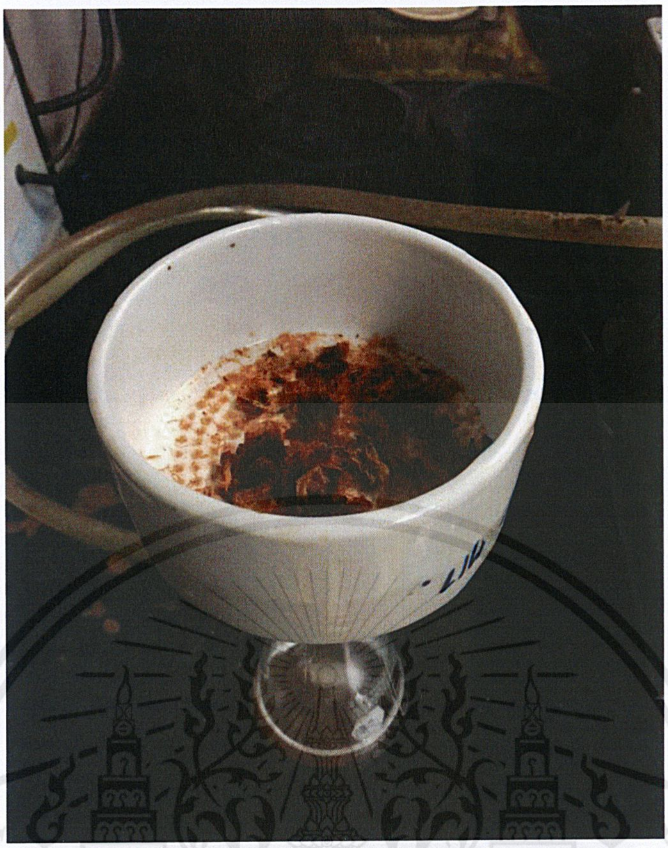

Figure D.3 Neutralization of cellulose by vacuum filter

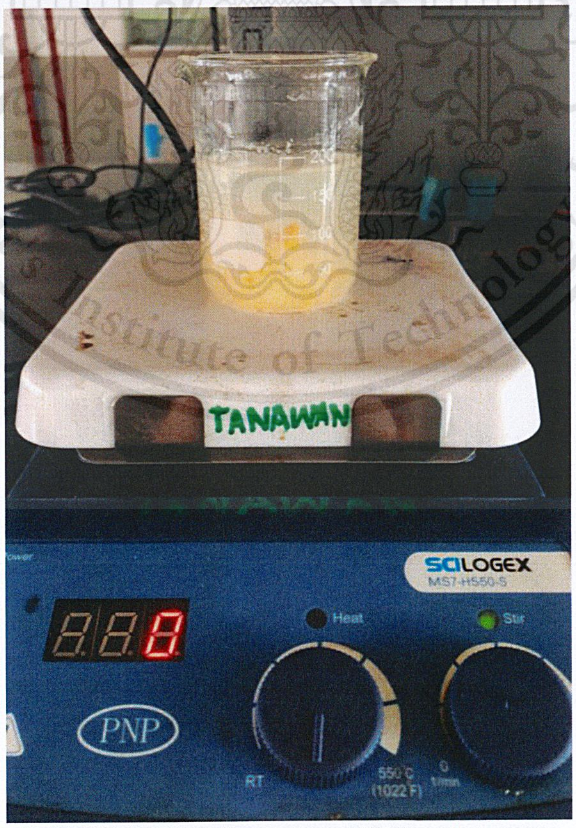

Figure D.4 Bleaching of the cellulose

Figure D.5 Filter the cellulose with vacuum filter

Figure D.6 Cellulose after extraction

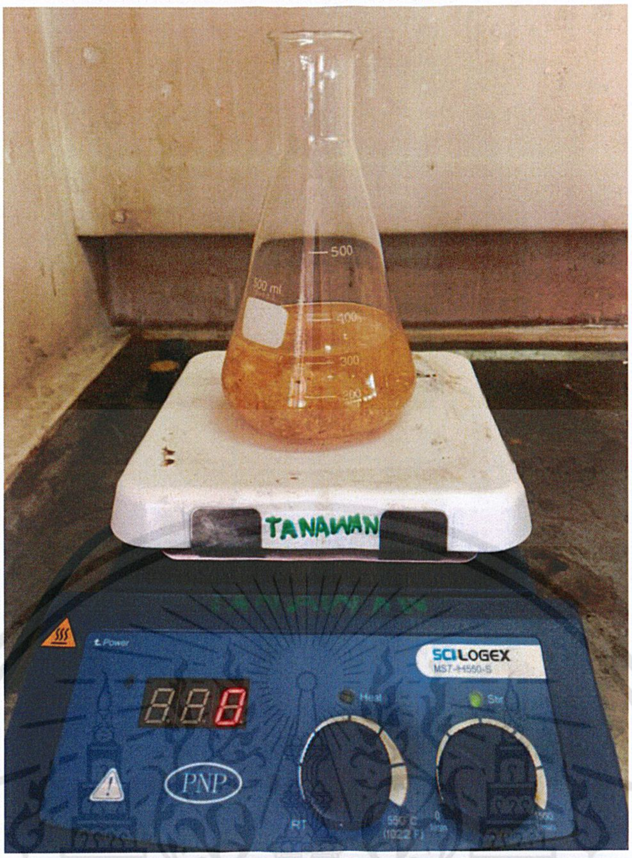

Figure D.7 Alkalization

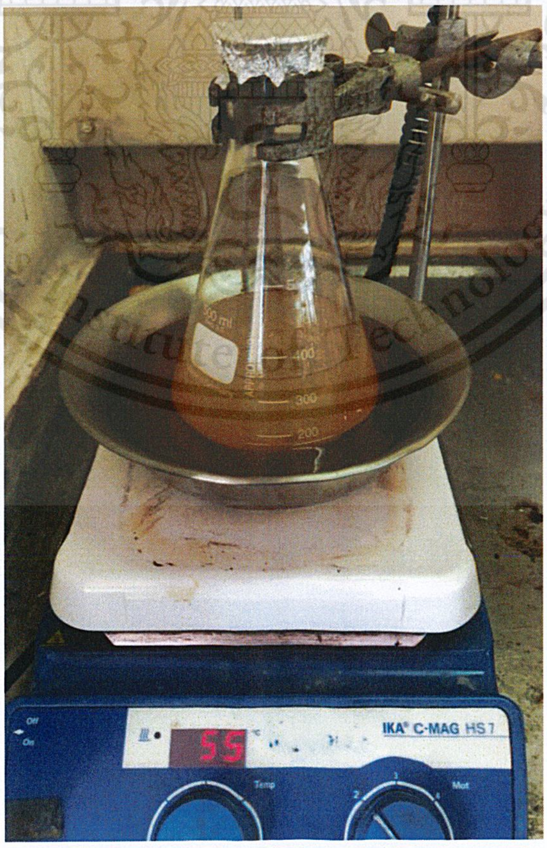

Figure D.8 Carboxymethylation

Figure D.11 Carboxymethyl cellulose from durian rind

BIOGRAPHY

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