Utilization of Cocoa (*Theobroma cacao* L.) pod husk as fillers for bioplastic from Jackfruit (*Artocarpus heterophyllus*) seed starch with Ethylene Glycol Plasticizer

Maulida*, Siti Maysarah and Jose
Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan 20155, Indonesia

*Email: maulida@usu.ac.id*

Abstract. Bioplastic is environmentally friendly plastic designed to facilitate the degradation of enzymatic reactions of microorganisms such as bacteria and fungi. This research was aimed to obtain the effect of cocoa pod husk addition on mechanical properties of bioplastics included tensile strength, elongation at break, functional group using FT-IR, surface morphology using SEM and biodegradation. Cocoa pod husk is a filler in production of bioplastic research. The production of bioplastic method that used in this research was casting method. Variation of jackfruit seed starch and cocoa pod husk composition ratio were 5:5, 6:4, 7:3, 8:2, and 9:1 (w/w) and variation of ethylene glycol were 0,2; 0,25; 0,3; 0,35; and 0,4 (v/w). The best condition of bioplastic was composition ratio of jackfruit seed starch and cocoa pod husk 7:3 on addition of ethylene glycol was 0,2 (v/w) with tensile strength 15,40 MPa, elongation at break 1,24%. From the result of FT-IR analysis indicated O-H group, C-H group, C=O group and C-O group on bioplastics. The result of mechanical properties were supported by Scanning Electron Microscopy (SEM) showed the bioplastic with cocoa pod husk as filler and ethylene glycol as plasticizer have the fracture surfaces were compact. From the result of biodegradation test, bioplastics was completely degraded within 14 days in the soil.

1. Introduction

Modern human life cannot be separated from plastic usage. Starting from the fulfillment of primary human needs, such as cutlery or food packaging, to tertiary needs, such as accessories for communication tools [1]. Conventional plastic which is still often used today is derived from synthetic polymeric materials made from petroleum, or natural gas that is difficult to be recycled and decomposed by decomposers. This can lead to environmental pollution in the form of soil, water and air pollution, as well as the accumulation of plastic waste.

These negative impact can be reduced by replacing conventional plastic base materials into materials that can be easily decomposed, called biodegradable plastics (bioplastics). Another benefit of bioplastics is very clear, such as reducing the amount of plastic waste. This biodegradable plastic is designed to facilitate the degradation process of enzymatic reactions of microorganisms such as bacteria and fungi [2]. One ingredient which is easily decomposed is starch. Starch is a promising material for plastic materials because it is universally renewable, and affordable [3].

The starch used for this study was starch derived from jackfruit seeds. Jackfruit (*Artocarpus heterophyllus*) is a tropical fruit that is widely grown in Asia, including in Indonesia. Based on data from the Central Statistics Agency of the Republic of Indonesia, jackfruit production in Indonesia in
2011 reached 652,981 tons [4]. Generally, the use of jackfruit tends only to the flesh of the fruit, while the seeds are mostly only thrown away as waste. Jackfruit seeds have a high starch content so that it can be used as an alternative for producing starch [5]. The starch content is the raw material for making bioplastics.

Some types of plasticizers from the polyol group include glycerol, ethylene glycol (EG), propylene glycol (PG) and polyethylene glycol (PEG) which are most often used as additives for polymers [6] [7]. In addition, starch is added with plasticizer to obtain stronger, flexible and slippery plastics [8].

This study aims to determine the effect of adding cocoa pod husk to the characteristics of bioplastic from jackfruit seed starch, including tensile strength, elongation at break time, functional group characteristics and morphological characteristics, and determine the rate of biodegradation of bioplastics produced.

2. Materials and methods

The research was conducted at the Pharmacy Research Laboratory in Faculty of Pharmacy, Chemical Engineering Operations Laboratory and Research Laboratory in Department of Chemical Engineering, Faculty of Engineering, University of Sumatera Utara, Medan. This research was conducted for approximately 6 months.

2.1. Equipment and materials

Equipments used in making bioplastics include: blenders, furnace, 110 °C thermometers, test tubes, beaker glass, porcelain cups, oven, magnetic stirrer, measuring cups, 100 and 200 mesh sieves, dropper pipettes, glass funnels, knife, filter paper, filter, erlenmeyer, hot plate, analytical balance, desiccator, stir bar, and bioplastic mold. Equipments used in analyzing bioplastic characteristics include: Universal Testing Machine and Shimadzu Prestige-21 IR. In this research the materials used include: cocoa pod husk, jackfruit seeds, aquadest (H_2O), ethylene glycol, NaOH, and lime water (CaCO_3).

2.2. Methods

The procedure for preparing cocoa pod husk is as follows [9]: Cocoa pod husk is washed with water to remove impurities. Every 5 kg of cocoa pod husk is cut to size ± 2 cm². Then pieces of cocoa pod husk soaked in lime water (CaCO_3) for 6 hours with a concentration of 1% where the lime water is a mixture of grams of lime (CaCO_3) in 2 liters of clean water. Lime water is used to remove the sap from the cocoa pod husk. After that the pod husk is dried in the sun for 6 hours to dry. Cocoa pod husk that has dried, blended until smooth. Blended cocoa pod husk are sieved with a 200 mesh sieve.

The procedure for making bioplastic is as follows [10]: The desired mass of jackfruit seed starch and cocoa shell is weighed with a variation ratio of 5:5, 6:4, 7:3, 8:2, 9:1 of the total dry weight of jackfruit seeds starch - cocoa pod husk as much as 10 grams. Then a starch solution is made with a ratio of starch: distilled water 1:20 and cocoa pod husk is inserted into a beaker glass. Beaker glass containing starch solution was heated while stirring using a stirrer for 10 minutes then ethylene glycol added with a volume variation of 0.2 ml; 0.25 ml; 0.3 ml; 0.35 ml and 0.4 ml. The mixture is then heated while stirring until it reaches a temperature of 88.135 °C. 20 ml of 5% w/v NaOH solution was added. Then stirring for 20 minutes. The mixture is then cooled and printed on acrylic molds with a size of 25 x 25 x 3 mm. The plastic is dried in an oven at 60 °C for 24 hours. The plastic is removed from the oven and then left at room temperature until the plastic can be removed from the mold.

2.3. Analysis of jackfruit seed starch characteristics

Starch content analysis is to determine the starch content in jackfruit seed starch. Starch content analysis was conducted at the Laboratory of Food Technology and Agricultural Products, Gadjah Mada University. Amylose content analysis is to determine the amylose content in jackfruit seed starch which generally gives strength properties to a film. Amylose content analysis was conducted at the Laboratory of Food Technology and Agricultural Products, Gadjah Mada University. Analysis of amylopectin levels is to determine the amylopectin content found in jackfruit seed starch which
generally gives a low mechanical properties in a film. Amylopectin content analysis was carried out at the Laboratory of Food Technology and Agricultural Products, Gadjah Mada University. Water and ash content analysis is to determine the water and ash content found in jackfruit seed starch. This analysis was conducted at the Research and Technology Center and Industrial Standardization (Baristand), Medan.

2.4. Bioplastic product analysis

Tensile strength test measurements are based on ASTM D882 with the provisions of the Universal Testing Machine (UTM) model. Samples to be analyzed are: Bioplastic products without cocoa pod husk fillers and bioplastic products with cocoa pod husk fillers. Specimen sketch for tensile test can be seen in Figure 1 below:

![Figure 1. Tensile strength test specimen sketch](image)

Tensile strength is calculated by dividing the maximum force in Newton (or pound-force) by the minimum cross-sectional area in square meters (or square inches). Results are stated in pascal (or pound-force per square inch).

\[
Tensile \ strength, \ \sigma = \frac{Tensile \ force (F)}{Area (A)} \quad (1)
\]

Percent elongation at break is the percent elongation at the time of the break up of the test specimen. The measurement is carried out in the same way as the tensile strength, which is based on ASTM D882 with the provisions of the Universal Testing Machine (UTM) model [11]. Samples to be analyzed are: Bioplastic products without cocoa pod husk fillers and bioplastic products with cocoa pod husk fillers. The extension at the time of breaking up is stated as a percentage through the following calculation:

\[
Elongation \ (%) = \frac{Length \ at \ break - \ beginning \ length}{Beginning \ length} \times 100\% \quad (2)
\]

Samples to be analyzed by Scanning Electron Microscope (SEM) are in the form of: Bioplastic products without cocoa pod husk fillers and bioplastic products with cocoa pod husk fillers and ethylene glycol plasticizers. Samples to be analyzed with Fourier Transform Infra-Red (FTIR) are in the form of: pure bioplastics, bioplastic products with cocoa pod husk fillers and ethylene glycol plasticizer. Degradation on the soil is done by weighing each sample weighing 0.25 grams before placing it on the ground and weighing it every two days for twelve days. Biodegradation in the soil is done by weighing each sample weighing 0.25 grams. Bioplastic samples are buried in the soil by maintaining the stability of the temperature and humidity of the soil to a depth of 30 cm. Then, bioplastics which are buried in the soil are weighed each time unit. The bioplastic mass fraction is weighed once every two days for twelve days [1]. Samples are removed from the soil to be weighed dry. The equation below is used to calculate the residual weight fraction [1].

\[
\% \ Residual \ Weight = 100\% - \left(\frac{W_1 - W_2}{W_1}\right) \times 100\% \quad (3)
\]

In which :
\[W_1 = \text{sample weight on day-0 (gram)}\]
\[W_2 = \text{sample weight on day-2, 4, 6, 8 and 10 (gram)}\]

3. Results and discussions

The results will be discussed in 6 subsections, they are results of jackfruit seed starch extraction, results of the characterization of jackfruit seed starch, characteristics of the results of FTIR analysis of bioplastics without/with cocoa pod husk powder fillers and ethylene glycol plasticizers, characteristic
results from jackfruit seed starch bioplast, bioplastic biodegradation test results of jackfruit seed starch with cocoa pod husk powder and ethylene glycol plasticizer, and characteristics of surface and verdict morphological analysis of bioplastic.

3.1. Results of jackfruit seed starch extraction
In this research, starch used in making bioplastics is starch extracted from jackfruit seeds. Jackfruit seeds come from jackfruit traders in Langsa City, Aceh.

![Figure 2. (a) Jackfruit seed (b) jackfruit seed starch.](image)

The yield of starch obtained from the extraction of jackfruit seed starch was 22.3%, which from 100 grams of jackfruit seeds obtained 22.3 grams dry starch which was then the starch that had been obtained will be analysed. The resulting starch is white powder ± 100 mesh. The jackfruit seeds obtained are shown in Figure 2 (a) and the extraction results in the form of starch are shown in Figure 2 (b).

3.2. The results of the characterization of jackfruit seed starch
The results of the characteristics of jackfruit seed starch and starch quality standards according to Indonesia Industry Standards are presented in Table 1 below:

| Component         | Content (%) | Indonesia Industry Standards (%) |
|-------------------|-------------|-----------------------------------|
| Water content     | 6.04        | Max 14                            |
| Ash content       | 1.08        | Max 1.5                           |
| Starch content    | 84.21       | Min 75                            |
| -Amylose          | 29.19       | -                                 |
| -Amylopectin      | 55.01       | -                                 |

The characteristics of jackfruit seed starch analysed in this study consisted of water content, ash content, amyllose content and amylopectin content. These analysis were carried out at the Nutrition Food Laboratory, Faculty of Food Technology, Gadjah Mada University, Yogyakarta.

3.2.1. Starch content.
The purpose of starch content analysis is to determine the percentage of starch content found in jackfruit seeds. Starch content is the amount of starch contained in dry matter expressed in percent [12]. From the results of jackfruit seed starch analysis conducted at the Nutrition Food Laboratory, Faculty of Food Technology, Gadjah Mada University, Yogyakarta obtained starch content in jackfruit seeds by 84.215%. Based on starch quality standards according to the Indonesian Industry Standard (SII) (in Maulida, 2018), permitted starch levels are at least 75% [13].
3.2.2. Amylose and amylopectin content.
Amylose and amylopectin levels are the amount of amylose and amylopectin contained in starch that can be used as a reference in determining starch characteristics. The purpose of the analysis of amylose and amylopectin levels is to determine the ratio of the amount of amylose and amylopectin in jackfruit seed starch. The ratio of amylose and amylopectin will affect the ability of starch paste to gel, thicken or form films [14]. Amylose and amylopectin levels were tested at the Laboratory of Food Technology Test and Research Results, Gadjah Mada University. In jackfruit seed starch, amylopectin content was 55.01% and amylose content was 29.19%.

3.2.3. Ash content.
Ash content indicates the mineral content of an ingredient. The purpose of the ash content analysis is to look at the general quality of the material where the ash content is also closely related to foreign impurities. The higher the ash content of an ingredient, the higher the mineral content of that material [15]. The value of ash content obtained from jackfruit seed starch is 1.09%. Based on starch quality standards according to Indonesian Industry Standards, permitted ash content is a maximum of 15% [14].

3.3. Characteristics of the results of FTIR analysis of bioplastics without/with cocoa pod husk powder fillers and ethylene glycol plasticizers
FTIR functional group analysis is needed to determine the functional groups contained in bioplastics without/with cocoa pod husk powder fillers and ethylene glycol plasticizers, FTIR functional group analyzes were carried out using IR Prestige-21 Shimadzu.

Characteristics of functional groups with FT-IR are carried out at the Faculty Laboratory, University of Sumatera Utara. From the functional group analysis using FT-IR obtained the results of the spectrum in the form of graphs which can be seen in Figure 3. In Figure 3 there are wave numbers that are read by FT-IR devices in bioplastics without fillers and bioplastics filled with cocoa pod husk powder with ethylene glycol plasticizer. The wave numbers that are read are adjusted to the frequency of the available wave numbers to identify functional groups of bioplastics without fillers and bioplastics filled with cocoa pod husk powder with ethylene glycol plasticizer. Changes in wave numbers in the two samples are presented in Table 2.

![Figure 3. FTIR result (a) bioplastics without cocoa pod husk filler (b) bioplastics with cocoa pod husk powder fillers and ethylene glycol plasticizers.](image-url)
Table 2. Wave numbers in starch-ethylene glycol bioplastic and starch-ethylene glycol bioplastic with cocoa pod husk powder.

| Type of bond (cm\(^{-1}\)) | Bioplastic- starch-ethylene glycol | Bioplastic- starch-ethylene glycol-cocoa pod husk |
|-----------------------------|-----------------------------------|-----------------------------------------------|
| Group O-H                   | 3606.89                           | 3695.31                                       |
| Group C-H                   | 2746.63                           | 2873.94                                       |
| Group C=O                   | 1674.21                           | 1759.08                                       |
| Group C-O                   | 1176.58                           | 1188.86                                       |

From the results of FT-IR analysis on bioplastics without fillers, it can be seen the appearance of absorption peaks at the number 3606.89 cm\(^{-1}\) indicates the presence of O-H groups. Furthermore, the appearance of the absorption peak at wave number 2746.63 cm\(^{-1}\) indicates the presence of C-H groups. There is an absorption peak at wave number 1674.21 cm\(^{-1}\) which is the C=O group. The absorption peak at wave number 1176.58 cm\(^{-1}\) indicates the alcohol group, ether, carboxylic acid, C-O ester.

From the results of bioplastic FT-IR analysis with cocoa pod fillers and ethylene glycol plasticizer, it can be seen the appearance of absorption peaks at wave number 3695.31 cm\(^{-1}\) which is the presence of alcohol O-H groups. The absorption peak at wave number 2873.94 cm\(^{-1}\) is a C-H group. The appearance of the absorption peak at wave number 1188.86 cm\(^{-1}\) indicates the presence of C-O groups. The presence of OH groups and the presence of other functional groups contained in bioplastics such as carbonyl functional groups and ester functional groups make plastic break down easily.

3.4. The characteristic results from jackfruit seed starch bioplastic

3.4.1. Effect of addition of cocoa pod husk powder and ethylene glycol plasticizer on bioplastic tensile strength properties

The following graph in Figure 4 shows the effect of variations in cocoa pod husk powder filler, jackfruit seed starch and ethylene glycol plasticizer on the tensile strength of bioplastics. The highest value of tensile strength was obtained in the ratio of starch mass: cocoa pod husk powder which was 7:3 and ethylene glycol 0.2 ml/gr with a value of 15.40 MPa. While the lowest tensile strength value was obtained in the ratio of starch mass: cocoa husk powder which is 7:3 and ethylene glycol 0.4 ml/g with a value of 0.78 MPa.

![Figure 4. Effect of variants of cocoa pod husk powder, jackfruit seed starch and ethylene glycol plasticizer on the properties of bioplastic tensile strength.](image-url)
In Figure 4 can be seen the effect of adding cocoa pod husk powder, jackfruit seed starch and ethylene glycol plasticizer on the tensile strength of jackfruit seed starch bioplastic. In Figure 4, it can be seen that the addition of cocoa pod husk powder and jackfruit seed starch has fluctuations, as well as the addition of ethylene glycol plasticizer. The highest value of tensile strength was obtained in the ratio of starch mass: cocoa pod husk powder which was 7:3 and ethylene glycol 0.2 ml/gr with a value of 15.40 MPa. While the lowest tensile strength value was obtained in the ratio of starch mass: cocoa husk powder which is 7:3 and ethylene glycol 0.4 ml/g with a value of 0.78 MPa.

From Figure 4 a very high tensile strength value was obtained in ethylene glycol plasticizers with a concentration of 0.2 ml/gram compared to other ethylene glycol plasticizer concentrations. This is because when a small amount of plasticizer is added to a polymer, the plasticizer molecules will be dispersed into a lower configuration. Conversely, if too much plasticizer is added, the polymer molecules will also move more easily which results in intermolecular forces between chains decreasing resulting in a decrease in strength and plasticity of the polymer [16].

From Figure 4 on the starch: cocoa pod husk powder ratio there is a low tensile strength result. This can be caused by the use of NaOH as a solvent in making bioplastics. Based on the research of Muhammad Dasuki, et al., (2013) which states that the addition of NaOH affects the characteristics of the porang flour bioplastic film, but does not show differences in the functional groups formed. The greater the addition of NaOH, the tensile strength properties, elastic modulus, and degree of distortion of bioplastic films tend to decrease [17].

3.4.2. Effect of variations in cocoa pod husk powder filler and ethylene glycol plasticizer on elongation at break of bioplastics

Figure 5 shows the relationship between the addition of cocoa pod husk powder and ethylene glycol plasticizer to the elongation at break of jackfruit seed starch bioplastic. From the picture above, it can be seen that the highest elongation at break value is the addition of 1 gram of cocoa pod husk powder and ethylene glycol 0.4 ml/gram which is equal to 13.80% while the lowest elongation at break is the addition of 5 gram cocoa pod husk powder and ethylene glycol 0.2 ml/gram which is 1.24%.

Increasing the amount of cocoa pod husk powder can cause the elongation at break value of bioplastics to decrease. The percentage of elongation is inversely proportional to the addition of fillers, so the more fillers the percentage of elongation will decrease. The addition of plasticizers serves as a giver of elastic properties in bioplastics, so the more plasticizers given will increase the value of plastic extension [6].

![Figure 5](image_url)

**Figure 5.** Effect of variations in cocoa pod husk powder filler, jackfruit seed starch and ethylene glycol plasticizer on elongation at break of bioplastics.
3.5. Bioplastic biodegradation test results of jackfruit seed starch with cocoa pod husk powder and ethylene glycol plasticizer

This biodegradation test process is needed to study the level of resistance of bioplastic films produced in relation to the influence of microbial decomposition and soil moisture. The initial weight of each burial sample in the soil was 0.25 gram with 100% residual weight fraction on the 14th day with an average weight of 0 gram sample with 0% residual weight fraction. While the initial weight of each sample above ground is 0.25 gram with 100% residual weight fraction on the 14th day, the average weight of sample is 0.24 gram with 95% residual weight fraction.

![Graph showing biodegradation results](image)

**Figure 6.** Residual weight fraction of bioplastic film during burial in the soil and at the soil surface.

The method of burial in the soil causes bioplastics to decompose more quickly than above the soil surface, this can be caused by the activity of microorganisms or degradation of water absorption into bioplastics. Bioplastics that are buried in the soil are degraded by bacteria or other decomposers. Immersion of bioplastic composites will make starch polymers break down into small pieces until they disappear in the soil [17].

3.6. Characteristics of surface and verdict morphological analysis of bioplastic

The morphological characteristics of the verdict's surface are demonstrated by the Scanning Electron Microscopy (SEM) analysis. Figure 7 (a) shows the results of bioplastic morphological analysis without the addition of cocoa pod husk powder fillers with magnification 1000 times, it appears that jackfruit seed starch has not been well dispersed at the time of mixing, it appears that there are quite a lot of white spots on the surface that indicate starch particles hasn't been well dispersed.

![SEM images](image)

**Figure 7.** Morphological analysis results (a) without fillers and (b) with addition fillers.
Figure 7 (b) shows the results of SEM analysis of the surface of bioplastic products with the addition of cocoa pod husk powder fillers and ethylene glycol plasticizers with magnification 1000 times showing a structure that is less smooth but more compact and solid than bioplastics without fillers.

4. Conclusions
The characteristics of jackfruit seed starch analysis results obtained that starch content 84.215%, water content 7.7%, ash content 1.09%, amylose content 29.19%, and amyllopectin content 55.015%. Bioplastic spectrum of jackfruit seed starch without cocoa pod husk powder obtained by O-H, C-H, C=O and C-O groups. Bioplastic spectrum of jackfruit seed starch with cocoa pod husk powder obtained by O-H, C-H, C=O, C-O and N-H groups. The best results of the analysis of the tensile strength of bioplastic were obtained in the starch composition: 7:3 (w/w) cocoa pod husk powder and ethylene glycol 0.2 ml/gram with tensile strength of 15.40 MPa. The best results of the analysis of elongation at the time of breaking up the bioplastic were obtained in the cocoa pod husk powder formulation of 9:1 (w/w) and ethylene glycol 0.4 ml/gram which is 13.80%.

Reference
[1] Sahwan F L, Martono D H, Wahyono S and Wisoyodharmo L A 2005 Jurnal Teknologi Lingkungan 6 (1) 311-318.
[2] Avella and M 2009 Materials 2 911-925.
[3] Ma X, Chang P R, Yang J and Yu J 2009 Carbohydrate Polymers 75 472-478.
[4] Badan Pusat Statistik Republik Indonesia 2012 Produksi buah-buahan di Indonesia tahun 1995-2011.
[5] Purbasari, Aprilina, Ekky F A and Raizka K M 2014 Bioplastik Dari Tepung Dan Pati Biji Nangka Semarang: Universitas Diponegoro.
[6] Darni, Yuli., Herti U and Siti N A 2009 Prosiding Seminar Penelitian & Pengabdian Kepada Masyarakat. Lampung: Universitas Lampung.
[7] Wojciechowska P 2012 The Effect of Concentration and Type of Plasticizer on the Mechanical Properties of Cellulose Acetate Butyrate Organic-Inorganic Hybrids. Poland: The Poznan University of Economics.
[8] Rohimah, Siti and Iqbal A 2012 Pemanfaatan Selulosa dari Kulit Jagung (Zea mays) Untuk Produksi Plastik Biodegradable. Bandung: Politeknik Negeri Bandung.
[9] Maulida, Mara B H, Alfarodo, Anita M, Ginting M H S 2018 ARPN Journal of Engineering and Applied Sciences 13 (1) 240-244.
[10] AOAC (Association of Official Analytical Chemists) 1998 Official Method of Analysis. Ed ke-15. Washington DC: AOAC.
[11] Ohwoavworhua, Adelakin F O T A, Okhamafe A O 2009 International Journal of Green Pharmacy 70 97-104.
[12] Azmi H 2017 Pengaruh Penambahan Serat Ijuk Termodifikasi dan Plasticizer Glicerol Terhadap Karakteristik Bioplastik dari Pati Biji Alpukat (Persea Americana mill). Medan: Universitas Sumatera Utara.
[13] Amalia R 2013 Karakterisasi Fisikokimia Dan Fungsiional Tepung Komposit Berbahan Dasar Beras, Ubi Jalar, Kentang, Kadela, Dan Xanthan Gum. Medan: Universitas Sumatera Utara.
[14] Cohournisa, Susilo R F B and Nugroho W A 2014 Jurnal Bioproses Komoditas Tropis 2 (2).
[15] Marbun E S 2012 Sintesis Bioplastik dari Pati Ubi Jalar Menggunakan Penguat Logam ZnO dan Penguat Alami Selulosa. Depok: Universitas Indonesia.
[16] Astika I M, Lokantara I P, Karohika I M G 2013 Jurnal Energi dan Manufaktur 6 (2) 115-122.
[17] Yusmarlela 2009 Studi Pemanfaatan Plasticizer Glicerol dalam Film Pati Ubi dengan Pengisi Serbuk Batang Ubi Kayu. Medan: Universitas Sumatera Utara.