

# CHAPTER I

## INTRODUCTION

### 1.1 Background

Starch and its derivative products are multipurpose materials and are widely used in various industries, including beverages, processed food, paper, animal feed, pharmaceuticals, chemicals and also in non-food industries such as textiles, detergents, packaging and so on. In the food industry, starch is used as a gelling and encapsulating agent. In the paper industry, it is used as an additive such as wet-end for surface size and coating binders, adhesives, and glass fiber sizing (Chiu & Solarek, 2009).

Various variants of starch are based on structural differences, content of amylose, amylopectin, protein and lipid. In general, the main starch content, which is anhydroglucose polymer, includes amylose and amylopectin, both of which are bound by (1,4) bonds in linear segments, and (1,6) bonds at branching points. Amylopectin is the main content of starch, ranging from 70-80% and affects the physiochemical and taste of starch (Dona, Pages, & Kuchel, 2010).

The hydrolysis reaction is usually carried out using an acid catalyst such as HCl (hydrochloric acid). The material used for the hydrolysis process is starch. In Indonesia, there are many plants that produce starch. Plants such as rice, corn, cassava, tubers, sugar palm and so on (Baskar & G. Muthukumaran, 2008).

Starch and its derivatives are widely used in various types of industries, both in the food and non-food industries. In the non-food industry, starch is widely used in the metal, textile, cosmetic and pharmaceutical, paper, construction and mining industries. In the textile industry, starch is used as an adhesive. In addition, starch can also be used as an ingredient that reduces wrinkles on clothes. In the chemical sector, starch and its derivatives are widely applied to the manufacture of biodegradable plastics, surfactants, polyurethanes, resins, chemical compounds and pharmaceuticals (Yetti, M., Nazamid, 2007).

In other sectors, starch and its derivatives are used as detergents that are non-toxic and safe for the skin, binders, solvents, biopesticides, lubricants, dyes and flavors. In the food industry, starch is widely used as a thickener, colloid stabilizer, gelling agent, adhesive and water retaining agent. Especially for the food industry, starch is very important for the manufacture of baby food, cakes, puddings, milk thickeners, jelly candy, and the manufacture of dextrins (Hill, G.C, 1997).

## **1.2 Experiment Goals**

1. Studying the effect of variables on the starch hydrolysis reaction.
2. Calculate the reaction rate constant and analyze the effect of the variable on the reaction rate constant.

## **1.3 Experiment Benefits**

1. Students can determine the effect of variables on the starch hydrolysis reaction.
2. Students can calculate the reaction rate constant and analyze the effect of the variable on the reaction rate constant.

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Starch

Starch is a glucose homopolymer with  $\alpha$ -glucosidic bonds. Various kinds of starch are not the same, depending on the length of the C chain and the straight or branched chain of the molecule. Starch has two different ends, namely the non-reducing end with a free OH group attached to atomic number 4 and the reducing end with an anomeric OH group. The hydroxyl groups of straight chain polymers / straight sections of the parallel branch-shaped structure will associate through hydrogen bonds which promote the formation of starch crystals. Starch consists of 2 fractions that can be separated by hot water. The soluble fraction is called amylose and the insoluble fraction is called amylopectin. Amylose has a straight structure and amylopectin has a branched chain (Winarno, 2002).

#### 2.2 Amylose dan Amylopectin

Starch is a polysaccharide which is a glucose polymer, which consists of amylose and amylopectin. Amylose is a part of a linear polymer with  $\alpha$ -(1,4) bonded glucose units forming a linear chain. The degree of polymerization (DP) of amylose ranges from 500-6000 glucose units depending on the source. Amylopectin is a polymer of  $\alpha$ -(1,4) glucose units with side chain  $\alpha$ -(1,6) glucose units. The  $\alpha$ -(1,6) bonds of glucose units are very few in a starch molecule, ranging from 4–5%. However, the number of branched-chain molecules, namely amylopectin, is very large with a DP ranging from  $10^5$ - $3 \times 10^6$  glucose units and is the main component that can affect the physiochemical and taste of starch (Dona, Pages, & Kuchel, 2010).

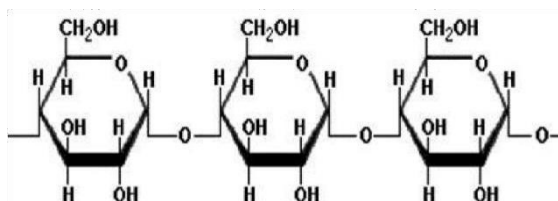


Figure 2.1 Amylose Structure

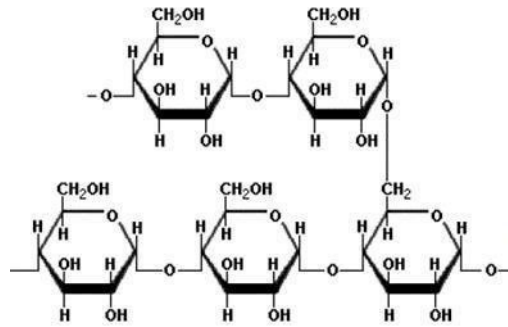
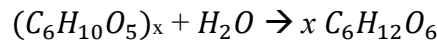


Figure 2.2 Amylopectin Structure

## 2.3 Starch Hydrolysis

Hydrolysis is a reaction that binds a hydroxyl group (-OH) by a compound. The OH group can be obtained from water. Hydrolysis can be classified into pure hydrolysis, acid-catalyzed hydrolysis, alkaline-catalyzed hydrolysis, alkaline combined hydrolysis with water and enzyme-catalyzed hydrolysis. Meanwhile, based on the reaction phase that occurs, it is classified into liquid phase hydrolysis and vapor phase hydrolysis.

Starch hydrolysis occurs between a starch reactant and water reactant. This reaction is first order, because excess water reactant is made, so the change in reactants is negligible. The starch hydrolysis reaction can be carried out using an  $H^+$  catalyst which can be taken from acid. The reactions that occur in starch hydrolysis are as follows :



Based on the theory of reaction rate :

$$-r_A = k \cdot C_{starch} \cdot C_{water} \quad (1)$$

Because the volume of water is quite large, it can be assumed that the concentration of water during the reaction change is equal to  $k'$ , so  $k'$  is equal to :

$$k' = k \cdot C_{water} \quad (2)$$

So equation 1 can be written as follows  $-r_A = k' \cdot C_{pati}$ . From this reaction rate equation, the hydrolysis reaction is a first order reaction. if  $-r_A = -\frac{dC_A}{dt}$ , then equation 2 becomes :

$$\frac{-dC_A}{dt} = k' C_A \quad (3)$$

$$-\frac{dC_A}{C_A} = k' dt \quad (4)$$

If  $C_A = C_{A0} (1 - X_A)$  and solved by integral and boundary conditions  $t_1 : C_{A0}$  and  $t_2 : C_A$  the equation becomes :

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k' \int_{t_2}^{t_1} dt \quad (5)$$

$$\ln \frac{C_{A0}}{C_A} = k' (t_2 - t_1) \quad (6)$$

$$\ln \frac{1}{(1-X_A)} = k' (t_2 - t_1) \quad (7)$$

Where  $X_A$  = reaction conversion after one second.

Equation 7 can be solved using the regression approach  $y = mx + c$ , with  $Y = \ln \frac{1}{(1-X_A)}$

dan  $x = t_2$ .

## 2.4 Starch Modification

Starch generally has a granular structure, is insoluble in water, and in this form is used only in a limited number of specific applications. Modifications are starches whose hydroxyl groups have undergone changes. Starch has the property of not being able to be used directly and therefore must be modified chemically or physically to increase the positive properties and reduce the undesirable properties. Starch is commonly used for food products, adhesives and glass fiber sizing. It is also added in plastics to speed up the degradation process. Chemical modification generally includes esterification, etherification, hydrolysis, oxidation and cross-linking (Chiu & Solarek, 2009). Modified starch will experience changes in properties that can be adapted for certain needs. However, just like natural starch, modified starch is insoluble in cold water (Koswara, 2009).

## 2.5 Influential Variable

Variables that influence the starch hydrolysis reaction include :

### 1. Catalyst

Almost all hydrolysis reactions require a catalyst to speed up the reaction. The catalyst used can be enzymes or acids because their performance is faster. The acids used are of various types such as HCl (Agra et al., 1973),  $H_2SO_4$  and  $HNO_3$ . What affects the rate of reaction is the concentration of  $H^+$  ions, not the type of acid. However, in industry generally used hydrochloric acid (HCl). This selection is based on the character of the salt formed on neutralization does not cause any disturbance other than a salty taste if the concentration is high. Therefore, the concentration of acid in the hydrolyzing water is kept as low as possible. Generally, an acid solution

that has a higher acid concentration is used than for syrup preparation. Hydrolysis at a pressure of 1 atm requires a much more concentrated acid.

## 2. Temperature and Pressure

The effect of temperature on the reaction rate follows the Arrhenius equation, where the higher the temperature, the faster the reaction rate. To achieve a certain conversion, it takes about 3 hours to hydrolyze yam starch at 100 °C. But if the temperature is raised to 135 °C, the same conversion can be achieved in 40 minutes (Agra et al., 1973). Hydrolysis of wheat and corn starch with H<sub>2</sub>SO<sub>4</sub> catalyst requires a temperature of 160 °C. Since the heat of reaction is close to zero and the reaction proceeds in the liquid phase, temperature and pressure have little effect on equilibrium.

## 3. Mixing (stirring)

In order for the reactants to collide with each other as well as possible, mixing is necessary. For batch processes, this can be achieved with the help of a stirrer or a whisk (Agra et al., 1973). If the process is a flow process (continuous), then the mixing is done by adjusting the flow in the reactor to form a swell.

## 4. Reagent ratio

If one of the reactants is made in excess, the balance can shift to the right. Therefore, the suspension of starch with a low concentration gave better results than the suspension with a high concentration. If the starch suspension content is reduced from 40% to 20% or 1%, the conversion will increase from 80% to 87% or 99% (Groggins, 1958). On the surface, the starch suspension content is high so that the reagent molecules will be difficult to move. To produce glucose, a starch suspension of about 20% is usually used.

## CHAPTER III

### PRACTICUM METHOD

#### 3.1 Tools and Materials Used

##### 3.1.1 Materials

1. Anhydrous glucose
2. Tapioca flour
3. NaOH
4. HCl
5. MB indicator
6. Fehling A
7. Fehling B
8. Aquadest

##### 3.1.2 Tools

1. Measuring cup
2. Thermometer
3. Erlenmeyer
4. Stands and Clamps
5. Burette
6. Boiling Threeneck
7. Volumetric flask

#### 3.2 Main Tool Image

Description:

1. *Magnetic stirrer + heater*
2. *Waterbath*
3. Boiling Threeneck
4. Thermometer
5. Condenser
6. Clamp
7. Stand

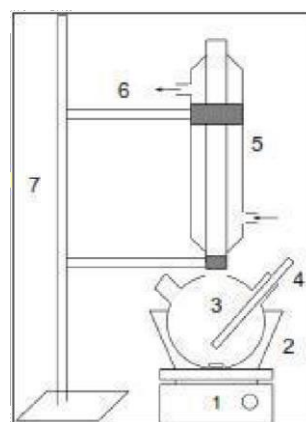


Figure 3.1 Hydrolysis Tools Equipment

### 3.3. Procedure

#### 1. Early preparation

##### a. Calculating starch density

Put 1 gram of starch with 5 ml of distilled water into a measuring flask, and note the change in volume

$$\rho_{\text{starch}} = \frac{m_{\text{starch}}}{\Delta V}$$

##### b. Calculating HCl density

Weigh the empty pycnometer ( $m_1$ ), put HCl into the pycnometer whose volume is known ( $v$ ), then weigh the weight ( $m_2$ ), then calculate the density of HCl.

$$\rho_{\text{H}_2\text{SO}_4/\text{HCl}} = \frac{m_2 - m_1}{V}$$

##### c. Standard glucose making

2 grams of anhydrite glucose is dissolved in 1000 ml of distilled water.

#### 2. Determination of starch content

##### a. Fehling's solution standardization

5 ml fehling A + 5 ml fehling B + 15 ml standard glucose, heated to boiling. After boiling, 3 drops of MB were added, then the solution was titrated with standard glucose until the color changed to brick red. Note the required volume of titrant (F), the titration process is carried out in a boiling state (on the stove).

##### b. Determination of initial starch content

A total of ... grams of starch, ... ml of HCl catalyst and ... ml of distilled water were put into a three-necked flask and heated to a temperature of ...°C for 1 hour. After that the solution was cooled, diluted with distilled water to 500 ml then 20 ml was taken and neutralized with NaOH (PH = 7). The solution is taken 5 ml diluted to 100 ml, after that take 5 ml of the solution. Put in 5 ml of the solution + 5 ml of fehling A + 5 ml of fehling B + 15 ml of standard glucose into the Erlenmeyer, then heated until boiling. Then add 3 drops of MB indicator. Then the solution is titrated with standard glucose so that the color changes to brick red. Note the required volume of titrant (M). Note this, the titration process is carried out in a boiling state on the stove. Do the same for the other variables.

##### c. Starch hydrolysis

A total of ... grams of starch, ... ml of HCl catalyst and ... ml of distilled water were put into a three neck flask and heated to a temperature of ...°C. Then after



5 minutes, take 20 ml of sample. Then the sample was neutralized with NaOH (PH = 7). The solution is taken 5 ml diluted to 100 ml, after that take 5 ml of the solution Put in 5 ml of the solution + 5 ml of fehling A + 5 ml of fehling B + 15 ml of standard glucose into the Erlenmeyer, then heated until boiling. Then add 3 drops of MB indicator. Then the solution is titrated with standard glucose so that the color changes to brick red. Note the required volume of titrant (M). Note this, the titration process is carried out in a boiling state on the stove. The sample was taken every 5 minutes 5 times, so a total of 25 minutes. (t<sub>1</sub>=5th minute, t<sub>2</sub>=10th minute, t<sub>3</sub>=15th minute, t<sub>4</sub>=20th minute, t<sub>5</sub>=25th minute). Do the same for variable 2.

The formula for determining the initial starch content =

$$X_{p0} = \frac{(F - M) \times N_{\text{glucose}} \times \frac{500}{\text{basis vol}} \times \frac{100}{5} \times 0,9}{W}$$

Where :

N = 0,002 gr/mL

W = starch weight

Calculation of reagent required:

a) Calculating HCl needed

$$V_{\text{HCl}} = \frac{N_{\text{HCl}} \times MW_{\text{HCl}} \times V_{\text{solution}}}{\rho_{\text{HCl}} \times \text{HCl content} \times 1000 \times \text{greq}}$$

Where :

HCl content = 0,25 for 25%

0,37 for 37%

greq HCl = 1

b) Calculating starch needed

$$\%_{\text{suspension}} = \frac{X_p \times W_{\text{starch}}}{W_{\text{starch}} + W_{\text{HCl}} + W_{\text{water}}}$$

Where :

$$W_{\text{starch}} = \rho_{\text{starch}} \times V_{\text{starch}}$$

$$W_{\text{HCl}} = \rho_{\text{HCl}} \times V_{\text{HCl}}$$

$$W_{\text{water}} = \rho_{\text{water}} \times (V_{\text{solution}} - V_{\text{starch}} - V_{\text{HCl}})$$

$$X_p = \frac{(F - M) \times N_{\text{glucose}} \times \frac{100}{5} \times 0,9}{W}$$

## BIBLIOGRAPHY

- Agra, I. B., Warnijati, S., dan Pujiyanto, B., 1973. “ Hidrolisa Pati Ketela Rambat Pada Suhu Lebih Dari 100 C”, Forum Teknik, 3, 115-129.
- Baskar, G., Muthukumaran, C., Renganathan, S., (2008), “Optimization of Enzymatic Hydrolysis of Manihot Esculenta Root Starch by Immobilize  $\alpha$ -Amylase Using Response Surface Methodology”, International Jurnal of Natural Sciences and Engineering 1:3, pp. 156-160.
- Chiu, C.-w., & Solarek, D. 2009. Modification of starch. *Starch: Chemistry and Technology, Third Edition ISBN: 978-0-12-746275-2*.
- Dona, A. C., Pages, G., & Kuchel, P. W. 2010. Digestion of starch: In vivo and in vitro kinetic models used to characterise. *Carbohydrate Polymers* 80(2010) 599– 617.
- Groggins, P. H. 1958. Unit Processes in Organic Synthesis, 5th ed. pp. 775 – 777, McGraw–Hill Book Company. New York.
- Hill, G.C., “An Introduction to Chemical Engineering Kinetika and Reactor Design”. 1nd ed, John Willey, New York, N.Y, 1977
- Koswara, S. 2009. *Teknologi Modifikasi Pati*. ebookpangan.com.
- Winarno, F.G., 2002. *Kimia Pangan dan Gizi*. PT. Gramedia Pustaka Utama, Jakarta.
- Yetti, M., Nazamid, B.S., Roselina, K. Dan Abdulkarin, S. M., (2007), “*Improvement of Glucose Production by Raw Starch Degrading Enzyme Utilizing Acid-Treated Sago Starch as Substrate*”, ASEAN Food Journal 14(2), pp. 83-90