

CHAPTER 1

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 et al., 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 & 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 et al., 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 dextrans (Hill, 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 α -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 and 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 α -(1,4) bonded glucose units forming a linear chain. The degree of polymerization of amylose ranges from 500-6000 glucose units depending on the source. Amylopectin is a polymer of α -(1,4) glucose units with side chain α -(1,6) glucose units. The α -(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 degree of polymerization ranging from 10^5 - 3×10^6 glucose units and is the main component that can affect the physiochemical and taste of starch (Dona et al., 2010).

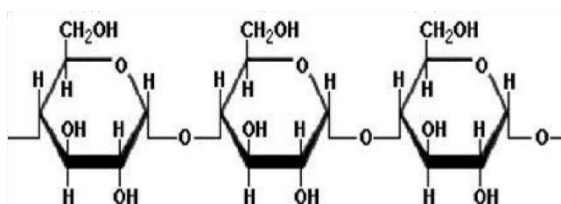


Figure 2.1 Amylose Structure

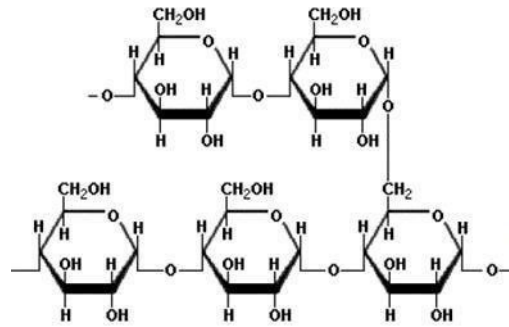
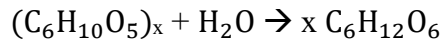


Figure 2.2 Amylopectin Structure

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 :

$$-r_A = k \cdot C_{\text{starch}} \cdot C_{\text{water}} \quad (2.1)$$

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 :

$$k' = k \cdot C_{\text{water}} \quad (2.2)$$

Equation 2.1 can be written as follows $-r_A = k' \cdot C_{\text{starch}}$. From this reaction rate equation, the hydrolysis reaction is a first order reaction. if $-r_A = -\frac{dC_A}{dt}$, then equation 2.2 become:

$$\frac{-dC_A}{dt} = k' C_A \quad (2.3)$$

$$-\frac{dC_A}{C_A} = k' dt \quad (2.4)$$

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 :

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k' \int_{t_2}^{t_1} dt \quad (2.5)$$

$$\ln \frac{C_{A0}}{C_A} = k' (t_2 - t_1) \quad (2.6)$$

$$\ln \frac{1}{(1-X_A)} = k' (t_2 - t_1) \quad (2.7)$$

Where X_A = reaction conversion after one second.

Equation 2.7 can be solved using the regression approach $y = mx + c$, with $Y = \ln \frac{1}{(1-X_A)}$

and $x = t_2$.

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 H₂SO₄ 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/H₂SO₄
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

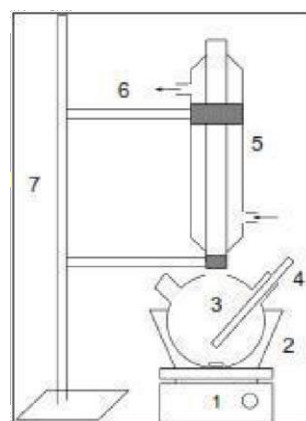


Figure 3.1 Hydrolysis Tools Equipment

3.3. Procedure

1. Early Preparation

a. Calculating starch density

In a measuring cup, 5 ml of distilled water is put in 1 gram of starch, note the volume change

$$\rho_{\text{starch}} = \frac{m_{\text{starch}}}{\Delta V} \quad (3.1)$$

b. Calculating HCl density

Weigh the empty pycnometer (m_1), put HCl/H₂SO₄ into the pycnometer whose volume is known (v), then weigh the weight (m_2), then calculate the density of HCl/ H₂SO₄.

$$\rho_{\text{H}_2\text{SO}_4/\text{HCl}} = \frac{m_2 - m_1}{V} \quad (3.2)$$

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/H₂SO₄ 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/H₂SO₄ 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. ($t_1=5$ th minute, $t_2=10$ th minute, $t_3=15$ th minute, $t_4=20$ th minute, $t_5=25$ th minute). Do the same for variable 2.

The formula for determining the initial starch content =

$$X_{p0} = \frac{(F-M) \times N_{\text{glucose}} \times \frac{500}{\text{basis vol}} \times \frac{100}{5} \times 0,9}{W} \quad (3.3)$$

Where :

$N = 0,002 \text{ gr/mL}$

$W = \text{starch weight}$

Calculation of reagent required:

a) Calculating HCl/H₂SO₄ needed

$$V_{\text{HCl}} = \frac{N_{\text{HCl/H}_2\text{SO}_4} \times MW_{\text{HCl/H}_2\text{SO}_4} \times V_{\text{solution}}}{\rho_{\text{HCl/H}_2\text{SO}_4} \times \text{HCl/H}_2\text{SO}_4 \text{ content} \times 1000 \times \text{greq}} \quad (3.4)$$

Where :

$\text{greq HCl} = 1$

$\text{greq H}_2\text{SO}_4 = 2$

b) Calculating starch needed

$$\%_{\text{suspension}} = \frac{X_p \times W_{\text{starch}}}{W_{\text{starch}} + W_{\text{HCl/H}_2\text{SO}_4} + W_{\text{water}}} \quad (3.5)$$

Where :

$$W_{\text{starch}} = \rho_{\text{starch}} \times V_{\text{starch}} \quad (3.6)$$

$$W_{\text{HCl/H}_2\text{SO}_4} = \rho_{\text{HCl/H}_2\text{SO}_4} \times V_{\text{HCl/H}_2\text{SO}_4} \quad (3.7)$$

$$W_{\text{water}} = \rho_{\text{water}} \times (V_{\text{solution}} - V_{\text{starch}} - V_{\text{HCl/H}_2\text{SO}_4}) \quad (3.8)$$

$$X_p = \frac{(F-M) \times N_{\text{glucose}} \times \frac{100}{5} \times 0,9}{W} \quad (3.9)$$

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IDENTIFIKASI BAHAYA DAN ANALISA RESIKO

MATERI : HIDROLISA PATI

IDENTIFIKASI BAHAYA (IB)											
A	Mekanik		D	Lingkungan		E	Bahan kimia		G	Bahaya lainnya	
A1	Penanganan manual		D1	Kebisingan		E1	Racun	√	G1	Gas terkompresi	
A2	Bagian yang bergerak		D2	Getaran		E2	Iritan	√	G2	Radiasi pengion	
A3	Bagian yang berputar		D3	Penerangan		E3	Korosif		G3	Radiasi UV	
A4	Pemotongan		D4	Kelembaban		E4	Karsinogenik		G4	Kelelahan	
B	Biologi		D5	Temperatur	√	E5	Mudah terbakar		G5	Ruang sempit	
B1	Bakteri		D6	Bahaya perjalanan		E6	Mudah meledak		G6	Penuh sesak	
B2	Virus		D7	Permukaan yang licin	√	E7	Cryogenics		G7	Termometer	
B3	Jamur		D8	Limbah padat		F	Peralatan				
C	Listrik		D9	Kualitas udara		F1	Bejana tekan				
C1	Voltase tinggi	√	D10	Pekerjaan soliter		F2	Peralatan panas	√			
C2	Listrik statis		D11	Percikan/tetes/banjir	√	F3	Laser				
C3	Kabel	√	D12	Tumpahan serbuk	√	F4	Pembuluh kaca				

DETAIL RESIKO							
IB	Resiko (setelah tindakan pengendalian)				Identifikasi resiko	Tindakan pengendalian untuk meminimalisir resiko	Tindakan pertolongan pertama
	Tinggi	Sedang	Rendah	Minimal			
1. PREPARASI/TAHAP AWAL							
D7, D11				√	Saat melakukan kalibrasi piknometer, dan pembuatan reagen-reagen, terdapat resiko aquadest tumpah yang menyebabkan permukaan menjadi licin.	Berhati-hati dalam menggunakan aquadest, jika aquadest dialirkan menuju tempat yang rawan terjadi tumpah, gunakan corong agar dapat meminimalisir terjadinya resiko permukaan licin.	Jika tergelincir, periksa bagian yang cidera dan obati bagian yang cidera. Apabila cideranya besar atau bertambah parah, bawa korban ke rumah sakit/ klinik terdekat.
D12				√	Saat melakukan perhitungan densitas pati, terdapat resiko dimana bubuk pati jatuh akan mengotori ruangan dan menyumbat saluran pernafasan apabila terhirup.	Hati-hati dalam memindahkan bubuk pati	Bersihkan serbuk pati yang jatuh. Apabila terhirup, sebisa mungkin keluarkan bubuk pati yang terhirup. Apabila cidera bertambah parah, bawa korban ke rumah sakit/ klinik terdekat
2. PERCOBAAN UTAMA							
C1, C3		√			Adanya kabel yang terlupas dan dapat mengakibatkan arus pendek maupun tersengat listrik.	Lakukan pemeriksaan dan memastikan alat secara baik.	Cabut sumber listrik untuk menghentikan aliran listrik.
D5, F2		√			Adanya kontak dengan kompor listrik atau alat yang dipanaskan diatas kompor listrik.	Hati-hati dengan permukaan panas pada saat melakukan proses pemanasan dan meletakkan rangkaian alat ke tempat yang lebih aman agar tidak terjadi kontak.	Hentikan proses pemanasan, dinginkan luka bakar, dan diberikan obat anti nyeri. Jika masih berlanjut, dibawa ke klinik atau rumah sakit terdekat.

DETAIL RESIKO							
IB	Resiko (setelah tindakan pengendalian)				Identifikasi resiko	Tindakan pengendalian untuk meminimalisir resiko	Tindakan pertolongan pertama
	Tinggi	Sedang	Rendah	Minimal			
E1, E2		√			Penggunaan reagen asam dan basa pada praktikum ini terdapat resiko kontak dengan kulit yang menyebabkan iritasi dan apabila tidak sengaja dikonsumsi dapat mengakibatkan keracunan.	Menggunakan sarung tangan lateks selama praktikum dan mengganti sarung tangan apabila sobek dan bolong serta berhati-hati dalam memindahkan reagen-reagen asam dan basa	Jika reagen terkena kulit, segera cuci tangan dengan air mengalir hingga bersih. Jika dikonsumsi, segera minum air mineral dan cuci mulut agar bahaya reagen dapat diminimalisir. Apabila bertambah parah, bawa korban ke rumah sakit/ klinik terdekat
3. ANALISA/TAHAP AKHIR							
D7, D11				√	Saat melakukan titrasi terdapat resiko larutan tumpah yang menyebabkan permukaan menjadi licin.	Berhati-hati dalam menggunakan aquadest, jika aquadest dialirkan menuju tempat yang rawan terjadi tumpah, gunakan corong agar dapat meminimalisir terjadinya resiko permukaan licin.	Jika tergelincir, periksa bagian yang cidera dan obati bagian yang cidera. Apabila cideranya besar atau bertambah parah, bawa korban ke rumah sakit/ klinik terdekat.