

CHAPTER I

INTRODUCTION

1.1 Background

Fats and oils are triglycerides or known as triesters of glycerol. The differences between fats and oils are that at room temperature, fats are solid and oils are liquid and oils contain higher percentage of unsaturated acids than fats. (Hart, 1983). Most of the glycerides in animals are fats which are commonly called animal fat, while the glycerides in plants tend to be in the form of oil and are referred to as vegetable oil.

Jatropha tree (*Ricinus communis*) is a source of renewable oil and is a non-edible oil so it does not compete with oils used for human consumption needs such as palm oil, corn oil, and others. The main product of the jatropha tree is the seeds, which can be extracted to produce castor oil when dried. Hydrolysis of castor oil into fatty acids and glycerols is carried out by heating a mixture of castor oil and a little sulfuric acid. Fatty acids obtained from the hydrolysis of an oil or fat generally have long and unbranched carbon chains.

The use of crude castor oil is limited to the tile industry, medicine, brake fluid, and slipper oil. The results of the hydrolysis of castor oil are commonly used for cosmetics, explosives, pharmaceutical industry, resin, textile industry, paper industry and as a solvent in the food and beverage industry. (Maharani, 2008).

1.2 Practice Objectives

After doing this experiment, practitioners are able to explain the following things:

1. The effect of catalyst concentration, temperature, type of catalyst, mole ratio of castor oil and water, hydrolysis time on conversion of hydrolysis of castor oil (x).
2. The effect of variable catalyst concentration, temperature, type of catalyst, ratio of moles of castor oil and water, hydrolysis time to the value of the rate constant for the hydrolysis reaction of castor oil (k).
3. The effect of catalyst concentration, temperature, type of catalyst, ratio of moles of castor oil and water, hydrolysis time to the direction of equilibrium of the hydrolysis reaction of castor oil (K).

1.3 Practice Benefits

1. Practitioners are able to understand the effect of catalyst concentration, temperature, type of catalyst, mole ratio of castor oil and water, hydrolysis time on conversion of hydrolysis of castor oil (x).
2. Practitioners are able to understand the effect of variable catalyst concentration, temperature, type of catalyst, ratio of moles of castor oil and water, hydrolysis time to the value of the rate constant for the hydrolysis reaction of castor oil (k).
3. Practitioners are able to understand the effect of catalyst concentration, temperature, type of catalyst, ratio of moles of castor oil and water, hydrolysis time to the direction of equilibrium of the hydrolysis reaction of castor oil (K).

CHAPTER II

LITERATURE REVIEW

2.1 Castor Oil

Castor oil is a vegetable oil obtained by pressing of the *Ricinus communis* seeds. The use of crude castor oil is limited to the tile industry, medicine, brake fluid, and slipper oil.

The physical properties of castor oil are colorless liquid or pale yellow in color, smell of fat, slightly biting taste, high viscosity and high acid number according to time which is indicated by damaged seeds and improper squeezing method. The chemical properties of castor oil is that it contains 46-53% oil. Castor oil contains 80% glycerides, asinolic acid, stearic isoeresinolate, dihydroxy stearate and palmiate. Castor oil also contains 20% protein, 0.2 toxic pyridine alkaloids, ricinin and the lipase enzyme. Castor oil contains the toxin substance ricin.

Castor oil extraction is done mechanically, using hydraulics at room temperature. Dry jatropha seeds were preheated using an autoclave at a temperature of 125-145°C for 30 minutes. Then the extraction process is carried out at a pressure of 200-400 kg/cm² for 5-15 minutes. The extraction result is crude castor oil, which requires further processing to be used for various industrial purposes (Lestiyani, 2000).

Table 2.1 Composition of fatty acid in castor oil

Type of fatty acid	Composition (%)
Ricinoleic acid	87,3
Oleic acid	4,69
Linoleic acid	4,92
Stearic acid	1,241
Palminic acid	1,016

(Yeboah *et al.*, 2021)

2.2 Castor Oil Hydrolysis

Hydrolysis is the binding of 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, and enzyme-catalyzed hydrolysis. Based on the hydrolysis reaction phase, hydrolysis can be classified into liquid phase and vapor phase.

Hydrolysis of castor oil to fatty acids and glycerol is carried out by heating the mixture of castor oil and a small amount of strong acid in a three neck bottle flask. Strong acid is needed as a catalyst because the hydrolysis reaction is very slow. Catalysts are not required if the hydrolysis is carried out at very high pressures of 700 psia and 485°F (Groggins, 1985) and the conversion achieved is >90%. In the hydrolysis process, water breaks down the alkyl groups in the triglycerides into fatty acids and glycerols. Heating is carried out to the desired temperature before hot water is added into the flask. Samples are taken every determined time (10 minutes) for free fatty acid analysis. The rate of hydrolysis is mainly determined by the rate of reaction between water and triglycerides in the oil phase. The use of excessive water allows the oil phase to always be saturated with water so that the hydrolysis reaction is pseudo-one-stage with respect to the concentration of glycerides. Generally, fatty acids produced by hydrolysis are unbranched chains and the number of carbon atoms is always even. If a double bond is present, it is usually in a cis (or Z) configuration and is not conjugated (Hart, 1983).

Reaction with water can possibly happen in the liquid phase and the oil phase (Lewkowitsch, 1903), but according to Lascaray (1949), the reaction in the oil phase is dominant, thus the reaction kinetic is determined by the rate of diffusion of water into the oil phase and the reaction between water and oil in the oil phase which can be presented into a mathematical equation.

a. The rate of diffusion of water into the oil phase

$$-r_A = k_{1a} (C_A^* - C_{A1}) \text{ mgreq/gr oil/min} \quad (2.1)$$

where:

C_A = concentration of water in the oil phase in equilibrium to the concentration of water in the aqueous phase or $C_A^* = k \cdot C_{A2}$

C_{A1} = concentration of water in the oil phase (mgreq/gr oil)

C_{A2} = concentration of water in the liquid phase

k_{1a} = rate of diffusion of water to the oil phase constant (min)

b. Rate of reaction in the oil phase

$$r_A = r_B = k_r \cdot C_{A1} \cdot C_B \quad (2.2)$$

where:

C_{A1} = concentration of water in the oil phase

C_B = concentration of oil/triglycerides

c. Mass balance of water in the oil phase

To find the step that controls the reaction kinetics, mass balance of is put out as follows:

$$\frac{dC_{A1}}{dt} = k_{1a}(C_A^* - C_{A1}) - k_r C_{A1} C_B \quad (2.3)$$

Assumption: with stirring, the mass transfer rate in the equation above $[(k_{1a}(C_A^* - C_{A1}))]$ is assumed much greater compared to the chemical reaction rate $[k_r \cdot C_{A1} \cdot C_B]$ so it is considered that only the rate of chemical reaction determines the rate of the overall reaction.

d. Mass balance of oil in the oil phase

$$\frac{dC_{A1}}{dt} = -k_r C_{A1} C_B \quad (2.4)$$

With the assumption that the reaction is first order, then one of the reactants is made excess. If the amount of water is excessive and the mass transfer of water to the oil phase is very fast, then the oil phase is considered to be always saturated with water, then $C_{A1} = C_A'$ which is constant at a certain temperature, $k_1 \cdot C_{A1} = k'$ so $-r_B = k' \cdot C_B$.

$$\begin{aligned} \frac{dC_{A1}}{dt} &= \frac{dC_B}{dt} = -k' C_B \\ \int_{C_{B0}}^{C_B} \frac{C_B}{C_{B0}} &= -k' \int_0^t dt \\ \ln \frac{C_B}{C_{B0}} &= -k' t \end{aligned} \quad (2.5)$$

where:

C_{B0} = the initial amount of triglycerides, mgreq/gr oil

C_B = the amount of triglycerides at a certain time = C_{B0} – the amount of free fatty acids formed, mgrek/g oil

If $X = \frac{\text{the amount of free fatty acids formed}}{\text{the initial amount of triglycerides}}$, then

$$X = \frac{C_{B0} - C_B}{C_B}$$

$$\frac{C_B}{C_{B0}} = \frac{C_{B0} - (C_{B0} - C_B)}{C_{B0}} = (1 - X) \quad (2.6)$$

$$\ln(1 - X) = -k' t \quad (2.7)$$

where:

k = first-order rate constant, s^{-1}

t = time of the reaction, s

The value of chemical reaction rate constant as a function of temperature can be expressed by the Arrhenius equation:

$$k = A e^{-\frac{E_a}{RT}} \quad (2.8)$$

where:

k = first-order rate constant, s^{-1}

T = temperature, K

where:

k = reaction rate constant, s^{-1}

T = absolute temperature, K

R = gas constant = 1,987 cal/gmol K

3. Catalyst

Catalyst is a substance added to a reaction to increase the rate of the reaction. The purpose of a catalyst is to increase the speed of the reaction (accelerate the reaction) by reducing the activation energy of a reaction. The lower the activation energy, the faster the reaction can take place at the same temperature. Catalysts that can be used are enzymes, acids, bases, salts, and ion exchangers. The catalyst chosen in this experiment is acid catalyst. The more acid catalyst is added, the greater the conversion as well as the reaction rate constant. When the catalyst is added, the more triglyceride molecules are activated.

According to Rahayu (1999), the relation between reaction rate constant (Kc) and acid concentration (c) mg mol H_2SO_4 / gr oil can be expressed by the equation:

$$Kc = 0,14525 c^{13} \quad (2.10)$$

with c = mg mole of H_2SO_4 / gr oil

Catalyst can lower the activation energy (E_a) by changing the process mechanism. Catalyst decreases E_a by increasing the intermediate energy so that the energy needed to become a product is lower (Kurniawan, 2012).

4. Stirring

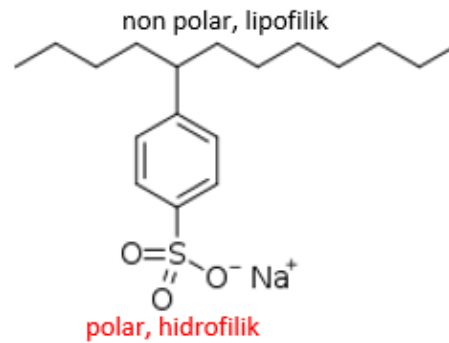
In order for substances to collide with each other properly, it is necessary to do stirring. For batch processes, this can be achieved with the aid of a stirrer. If the process is continuous, the stirring is done by adjusting the flow in the reactor so that agitation occurs. The reaction can run well if the solution is mixed properly. Stirring can reduce the mass transfer resistance and speed up the diffusion of the reactants (Fogler, 1999).

5. Ratio of Reactants

If one of the reactants is made excess, the equilibrium can shift to the right and if the products are taken, the reaction will also shift to the right, increasing the frequency of collisions, so that the reaction rate constant increases (Kirk & Othmer, 1980).

2.5 The Effect of Surfactant

The surfactant used in castor oil hydrolysis is an emulsifier in the form of soap. Surfactant molecules have hydrophilic and lipophilic groups so that they can unite a mixture of oil and water, hydrophilic (water-loving) and lipophilic (oil-loving) molecules. In general, the nonpolar (lipophilic) part is a long alkyl chain and the polar (hydrophilic) part contains a hydroxyl group (Hart, 1983).



Picture 2.2 The formula of surfactant

In the surfactant molecule one of the groups must be dominant in number. If the polar group is more dominant, the surfactant molecules will be absorbed more strongly into water than oil. As a result, the surface tension decreases so that the two phases easily spread and become a continuous phase. On the other hand, if the non-polar group is dominant, the surfactant molecules will be absorbed more strongly by the oil than the water (Zuhrina, 2010).

2.6 The Usage of Ethanol

Ethanol, also known as ethyl alcohol, which is better known in the market as alcohol, is an organic compound with the chemical formula C₂H₅OH. Under ambient conditions, ethanol is a volatile, flammable and colorless liquid (Safaatul & Prima, 2010).

The function of alcohol is to liquitate cells that contain oil and dissolve the oil, as described in the Journal of Safaatul M. & Prima A.H. in 2010 regarding the extraction of kaffir lime leaf oil (*Citrus hystrix DC*) with ethanol and n-hexane as solvents, that the requirements for a compound to be used as a solvent are must be inert, can dissolve but do not react with oil components, the solvent has a fairly low boiling point so that the solvent is easily evaporated without using high temperatures.

BAB III

RESEARCH METHODOLOGY

3.1 Experimental Design

3.1.1 Experimental Scheme

3.1.2 Variables

- a. Control variables
 1. Volume of mixture :
 2. Volume of emulsifier :
 3. Time interval :
 4. NaOH concentration :
 5. Titration temperature :
 6. H₂SO₄/HCl concentration:
- b. Independent variables
 - Catalyst concentration
 - Temperature
 - Type of catalyst
 - Mole ratio of castor oil and water
 - Hydrolysis time

3.2 Materials and Tools Used

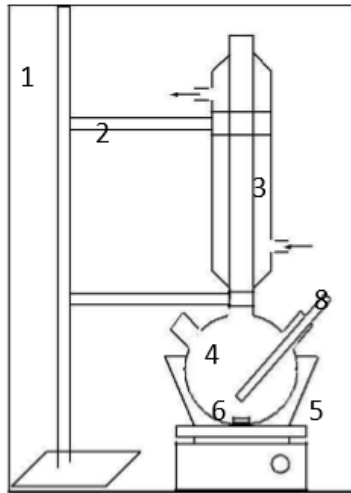
3.2.1 Materials

- a. Castor Oil ... ml
- b. Aquadest
Using H₂O from the Reverse Osmosis (RO) process ... ml.
- c. Catalyst
Catalyst used is H₂SO₄ with 98% purity or HCl ... N ... ml.
- d. NaOH
Using technical grade NaOH in the form of crystals and white in color, produced by PT. BRATACO CHEMIKA ... gram.
- e. Alkohol
Using ethanol or methanol with ...% purity ... ml.
- f. Surfactant
Using Sunlight produced by PT. UNILEVER Tbk. ... ml.
- g. Indicator of titration
Using 3 drops of PP.

3.2.2 Tools

- a. Three neck bottle flask
- b. Stative
- c. Clamp
- d. Burette
- e. Heater, magnetic stirrer
- f. Thermometer
- g. Condenser
- h. Waterbath
- i. Erlenmeyer

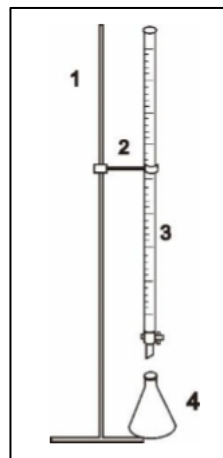
3.3 Picture of the Tools



Gambar 3.1 Series of hydrolysis equipment

Description:

- 1. Stative
- 2. Clamp
- 3. Condenser
- 4. Three neck bottle flask
- 5. Waterbath
- 6. Magnetic stirrer
- 7. Heater
- 8. Thermometer



Gambar 3.2 Series of titration equipment

Keterangan:

- 1. Stative
- 2. Clamp
- 3. Burette
- 4. Erlenmeyer

3.4 Response Test Results

The response measured is in the form of free fatty acid levels formed as a result of the hydrolysis of castor oil, so that the amount of conversion, reaction rate constant and equilibrium constant can be determined.

3.5 Procedures

A. Density Measuring

- Density of Castor Oil

Weigh the empty pycnometer (m_1), put castor oil into the pycnometer with known volume (V), weigh the weight (m_2). Calculate the density of castor oil.

$$\rho = \frac{m_2 - m_1}{V} \quad (3.1)$$

- Densitas Katalis

Weigh the empty pycnometer (m_1), put technical grade HCl into the pycnometer with known volume (V), weigh it (m_2). Calculate the density of the HCl catalyst. Do the same for H_2SO_4 catalyst.

B. Analysis of Free Fatty Acid Content in Crude Oil

1. Put ... ml of castor oil into the erlenmeyer.
2. Add ... ml of solvent and heat it while stirring at the temperature of ... °C.
3. Add 3 drops of PP indicator and titrate the solution with NaOH until the color of the solution turns pink.
4. Write down the volume of titrant needed.

C. Castor Oil Hydrolysis

1. Put castor oil into the three neck bottle flask.
2. Put the catalyst into the three neck bottle flask.
3. Flow cooling water during the hydrolysis process.
4. Heat the solution to the temperature of ... °C, then add heated aquadest and emulsifier into the three neck bottle flask.
5. Take sample in an interval of ... minutes to analyze the amount of fatty acid formed for ... minutes.

D. Analysis of Free Fatty Acid Content After Hydrolysis

1. Put ... ml of the hydrolyzed castor oil into the Erlenmeyer
2. Add ... ml of solvent dan heat the solution while stirring at the temperature of ... °C
3. Add 3 drops of PP indicator and titrate the solution with NaOH until the color of the solution turns pink.
4. Write down the volume of titrant needed.
5. Repeat the hydrolysis steps and analyze the free fatty acid content of the hydrolysis results according to the variables.

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