CHAPTER I
INTRODUCTION

1.1 Background

Along with the development of scientific and technological progress in the Indonesian industrial sector, various industries continue to innovate and develop, one of which is the chemical industry. These developments increase the production needs of the chemical industry, both for raw materials and other supporting materials. The raw materials and supporting materials in the chemical industry are very diverse. One of the materials used is ethyl acetate which is a type of solvent with the molecular formula $CH_3COOC_2H_5$.

Esterification is a reaction to form an ester from a carboxylic acid and an alcohol. The reaction products are esters and water. The general equation for this reaction can be determined as follows:

$$R\text{-}COOH + HO\text{-}R^* \; R\text{-}COOR^* + H_2O$$

The esterification reaction is a reversible, exothermic reaction, and runs very slowly but when using a mineral acid catalyst such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) equilibrium will be achieved in a fast time (Susanti, 2019). Therefore, it is necessary to study the influencing factors and conduct various experiments to determine the various process variables that affect the esterification process.

1.2 Practical Purpose

1. Knowing the effect of reaction time on the conversion of esterification reactions.
2. Knowing the effect of the variable on the conversion in the esterification process.
3. Knowing the effect of the variable on the reaction rate constant (k) in the esterification process.
4. Knowing the effect of the variable on the direction of equilibrium (K) in the esterification process.

1.3 Practicum Benefits

1. Students can understand how the effect of reaction time on conversion in the esterification process.
2. Students can determine the effect of a certain variable on the conversion of the ester formed.

3. Students can find out how to observe the effect of a certain variable on the direction of the equilibrium (K) and the reaction rate constant (k).
4. Students can conduct numerical studies based on the experiments carried out.

CHAPTER II
LITERATURE REVIEW

2.1 Kinetics Reaction

Esterification is a reaction between a carboxylic acid and an alcohol with the product are ester and water. An example is the reaction between acetic acid and ethanol. The esterification reactions include the following:

$$\underset{A}{CH_3COOH} + \underset{B}{C_2H_5OH} \leftrightarrow \underset{C}{CH_3COOC_2H_5} + \underset{D}{H_2O}$$

Chemical reaction rate equation:

$$-r_A = \frac{-dC_A}{dt} = k_1[A][B] - k_2[C][D]$$

With:

$-r_A$ = reaction rate of formation ester

[A] = acetic acid concentration [CH_3COOH]

[B] = ethanol concentration [C_2H_5OH]

[C] = ethyl acetate concentration [$CH_3COOC_2H_5$]

[D] = water concentration [H_2O]

k_1 = reaction rate constant to the right (products direction)

k_2 = reaction rate constant to the left (reactants direction)

t = time reaction

Based on the kinetics reaction, the reaction speed of ester formation will increase with increasing temperature, stirring, and adding a catalyst. This can be explained by the Arrhenius equation:

$$k = Ae^{-E_A/RT}$$

With:

k = reaction rate constant (L/mol.waktu)

A = collision frequency factor

E_A = activation energy (J/mol)

R = universal gas constant (8,314 J/mol.K)

T = temperature (K)

Based on the Arrhenius equation, it can be seen that the reaction rate constant is influenced by the values of A, E_A, and T, the increase of the collision factor (A), will increase the reaction rate constant. The value of activation energy (E_A) is influenced by the use of a catalyst, catalyst will reduce the activation energy so that the value of k will increase. The higher the temperature (T), the value of k also getting bigger.

2.2 Thermodynamics Overview

Based on the thermodynamics overview, we can find out whether the reaction is reversible or irreversible by looking at the change in Gibbs energy ($\Delta G°$). The esterification reaction between acetic acid and ethanol occurs according to the following reaction:

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

$$\Delta H°_{298} = \Delta H°_f \text{ products} - \Delta H°_f \text{ reactants}$$

Known standar $\Delta H°_f$ data (Smith *et al.*, 2001) :

$\Delta H°_{f\,298}$ CH_3COOH = -484500 J/mol

$\Delta H°_{f\,298}$ C_2H_5OH = -277690 J/mol

$\Delta H°_{f\,298}$ $CH_3COOC_2H_5$ = -480000 J/mol

$\Delta H°_{f\,298}$ H_2O = -285830 J/mol

So :

$$\Delta H°_{298} = (\Delta H°_{f\,298}\, CH_3COOC_2H_5 + \Delta H°_{f\,298}\, H_2O) - (\Delta H°_{f\,298}\, CH_3COOH + \Delta H°_{f\,298}\, C_2H_5OH)$$

$$= (-480000 \text{ J/mol} - 285830 \text{ J/mol}) - (-484500 \text{ J/mol} - 277690 \text{ J/mol})$$

$$= -3640 \text{ J/mol}$$

Based on the thermodynamics overview, it can also be seen that the reaction is endothermic or exothermic by observing the enthalpy changes. From the calculation, the enthalpy change (ΔH) is negative which indicates that the esterification reaction of acetic acid with ethanol is exothermic.

$$\Delta G°_{298} = \Delta G°_f \text{ products} - \Delta G°_f \text{ reactants}$$

Known standar $\Delta G°_f$ data (Smith *et al.*, 2001) :

$\Delta G°_{f\,298}$ CH_3COOH = -389900 J/mol

$\Delta G°_{f\,298}$ C_2H_5OH = -174780 J/mol

$\Delta G°_{f\,298}$ $CH_3COOC_2H_5$ = -332200 J/mol

$\Delta G°_{f\,298}$ H_2O = -237129 J/mol

So :

$$\Delta G°_{298} = (\Delta G°_{f\,298}\, CH_3COOC_2H_5 + \Delta G°_{f\,298}\, H_2O) - (\Delta G°_{f\,298}\, CH_3COOH + \Delta G°_{f\,298}\, C_2H_5OH)$$

$$= (-332200 \text{ J/mol} - 237129 \text{ J/mol}) - (-389900 \text{ J/mol} - 174780 \text{ J/mol})$$

$$= -4649 \text{ J/mol}$$

From the Van't Hoff equation :

$$\Delta G°_{298} = -R.T.\ln K$$

$$\ln K = \frac{-\Delta G°_{298}}{RT}$$

$$\ln K = -\frac{(-4649)\ ^{J}/_{mol}}{8{,}314\ ^{J}/_{mol.K}\ (298\ K)}$$

$K \quad = 6{,}5240$

If in this practicum an operating temperature of 54°C is used, then the value of K at 54°C can be calculated:

$$\ln \frac{K}{K_{298}} = -\frac{\Delta H°_{298}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$$

$$\ln \frac{K_{327}}{6{,}5240} = -\frac{(-3640)\ {}^{J}/_{mol}}{8{,}314\ {}^{J}/_{mol.K}}\left(\frac{1}{327} - \frac{1}{298}\right)K$$

$$K_{313} = 5{,}7277$$

From the Gibbs energy calculation, the K value at an operating temperature of 54°C is obtained and a value of 5,7277 is obtained. So, it can be concluded that the esterification reaction of acetic acid with ethanol is a reversible reaction.

Calculating theoretical conversion value.

On operating temperature of 54°C the value of K = 5,7277 is obtained.

At equilibrium :

$$K = \frac{C_C C_D}{C_A C_B}$$

$$K = \frac{(C_{A0}X_A)(C_{A0}X_A)}{C_{A0}\,(1-X_A)(C_{B0}-(C_{A0}X_A))}$$

$$K = \frac{(X_{Ae})^2}{(1-X_{Ae})(1{,}5-X_{Ae})}$$

$$5{,}7277 = \frac{(X_{Ae})^2}{(1-X_{Ae})(1{,}5-X_{Ae})}$$

$$X_{Ae} = 0{,}8273$$

So that at equilibrium with an operating temperature of 54°C theoretically a conversion value of 82.73% is obtained (The above calculations are only examples, the practicant must adjust the reaction temperature and the mole ratio of reactants according to the temperature variable obtained in the practicum).

2.3 Reaction Mechanism

The esterification reaction is characterized by the formation of an ester from the reaction of a carboxylic acid and an alcohol (methanol or ethanol). This reaction takes place slowly at room temperature so that heating is needed and the use of a catalyst to speed up the reaction rate. Esterification reactions are generally used to process raw materials for biodiesel production to reduce the concentration of free fatty acids (Almeida *et al*., 2018).

During the process, esterification used either an acid or base catalyst. Esterification reaction is reversible (Salamah, 2014). In this experiment, a carboxylic acid in the form of acetic acid is reacted with an alcohol in the form of methanol using an acid catalyst. For the preparation of ethyl acetate, the esterification reaction that occurs in this experiment and the mechanism of acid catalysis in ester hydrolysis are as follows:

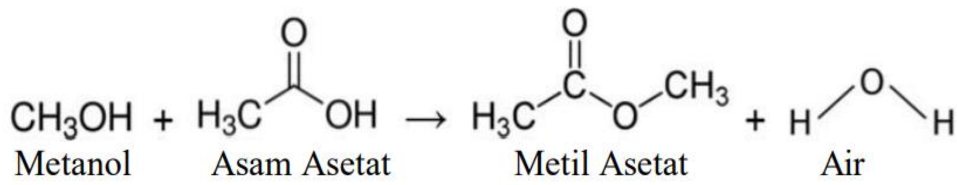


Figure 2.1 Esterification reaction

The mechanism of the esterification reaction is a substitution reaction between acyl nucleophiles with an acid catalyst (usually HCl or H_2SO_4). The carbonyl group of a carboxylic acid is not strong enough as an electrophile to be attacked by an alcohol. The acid catalyst will protonate the carbonyl group and activate it towards the nucleophile attack. The release of a proton will produce a hydrate from the ester, then proton transfer occurs.

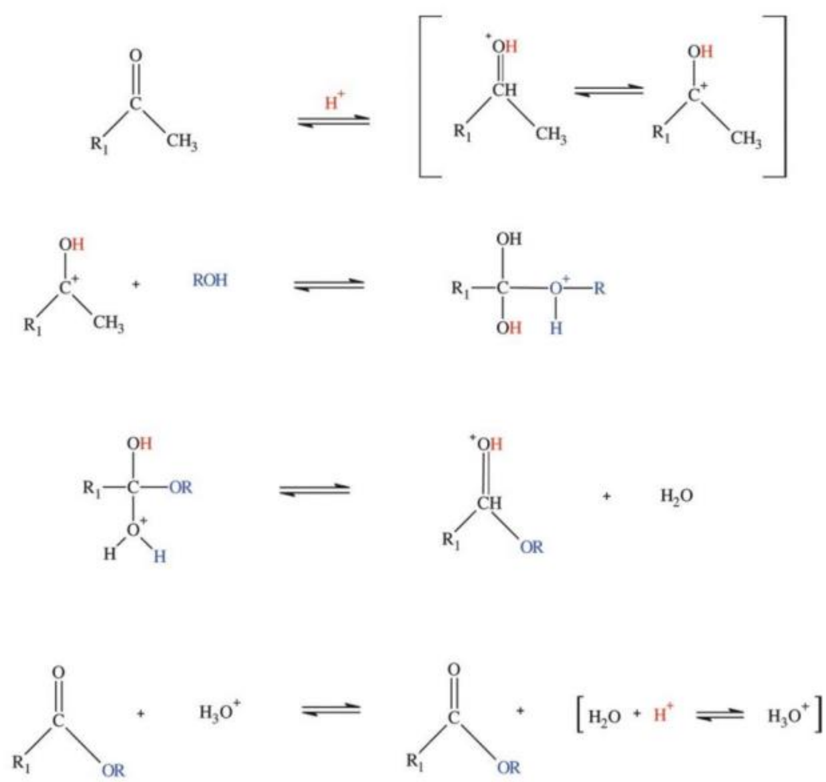


Figure 2.2 Mechanism of esterification reaction

The mechanism of esterification with an acid catalyst includes:

1. In the first step, the carbonyl group will be protonated by the acid. Transfer of protons from the acid catalyst to the carbonyl oxygen atom, resulting in an increase in the electrophilicity of the carbonyl carbon atom.
2. The second step involves the addition of a nucleophile, i.e. the OH group on the alcohol attacks the protonated carbonyl carbon. So a new C-O

bond (ester bond) is formed.

3. The third stage is the equilibrium stage in which the H^+ group is removed from the new ester bond. Deprotonation is carried out to form stable C-O bonds.
4. In the fourth step, one of the hydroxyl groups must be protonated, because the two hydroxyl groups are identical.
5. The fifth stage, involves breaking the C-O bonds and releasing water. In order for this event to occur, the hydroxyl group must be protonated so that its ability as a free group is better.
6. In the last stage, the protonated ester releases its proton.

2.4 Influential Variables

The esterification reaction is influenced by several variables. The variables in question are:

1. Reaction time

   The longer the reaction time, the longer the possibility of contact between substances so that higher conversion results. But when it reaches equilibrium, the reaction time will no longer affect the results obtained (Nurhayati *et al*., 2017).

2. Ratio of reactants

   The mole ratio of acid and alcohol has a direct impact on the rate of esterification conversion (Kastratovic and Bigovic, 2018). This is due to the reversible nature of the reaction, so one of the reactants must be made so that the reaction tends to move towards the product so that more esters are produced.

3. Stirring

   Stirring in the reaction process has a positive impact on increasing the reaction speed. Where by stirring, the tendency of contact between reactants will be higher so that the reaction speed increases (Nuryoto *et al*., 2020). The optimum stirring speed for various raw materials needs to be adjusted based on their different physical properties (Panchal *et al*., 2020).

4. Temperature

   The higher the operating temperature, the faster the rate of reaction kinetics. This is in accordance with the Arrhenius equation which states that when the temperature increases, the value of the reaction rate constant will be greater, so that the reaction runs faster. However, because the esterification reaction is exothermic, the higher the temperature, the lower the final conversion obtained. In addition, high reaction temperatures are also avoided because of the possibility of methanol loss due to evaporation (Wendi *et al*., 2014).

5. Catalyst

According to Nuryoto *et al*. (2020) if the esterification process is carried out without a catalyst, the reaction will not be effective and efficient. So that the presence of a catalyst can accelerate the rate of reaction and can maximize the conversion of acetic acid. An increase in the amount of catalyst resulted in an increase in yield during the reaction time.

CHAPTER III
PRACTICUM METHOD

3.1 Experimental Design

3.1.1 Variable

A. Fixed variable

Types of carboxylic acid :

Total volume :

Titration sample volume :

Sampling time :

B. Changed variable

3.2 Materials and Tools Used

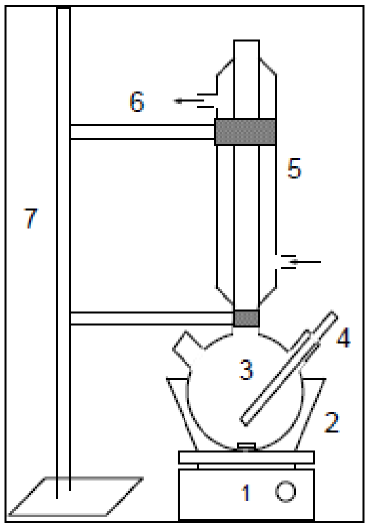
3.2.1 Materials

1. Acetic acid
2. Alcohol (ethanol)
3. Catalyst (HCl or H_2SO_4)
4. NaOH
5. PP indicator

3.2.2 Tools

1. Scale
2. Three-neck flask
3. Leibig condensor
4. Electric stove
5. Thermometer
6. Burette 50 mL
7. Measuring pipette
8. Drop pipette
9. Stative
10. Clamp
11. Erlenmeyer
12. Beaker glass
13. Volumetric flask
14. Aspirator

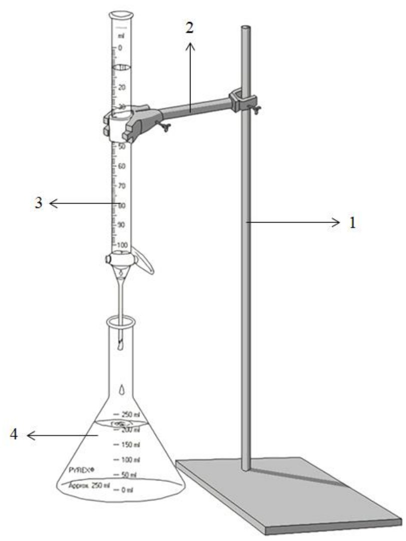
3.3 Toolkit Images



Where:

1. Magnetic Stirrer + heater
2. Waterbath
3. Three-neck flask
4. Thermometer
5. Leibig condensor
6. Clamp
7. Stative

Figure 3.2 Series of hydrolysis tools



Where:

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

Figure 3.3 Rangkaian alat titrasi

3.4 Procedure

A. Preparation

1. Calibrate the pycnometer by weighing the empty pycnometer and recording its mass, then filling it with aquadest, weighing it, and recording its mass.
2. Measuring the density of acetic acid, catalyst, and alcohol using a pycnometer. The pycnometer is filled with the reagent whose density you want to calculate, then weighing and recording its mass.
3. Calculate the density with this equation :

$$\rho = \frac{(mass\ pycno + reagent) - (mass\ empty\ pycno)}{volume\ pycno}$$

4. Weighing … gram of NaOH, then dissolve into 250 mL of aquadest.

After dissolving, put it in the burette to use as titrant.

B. Main Experiment

1. Assemble the tools as depicted in the figures above.
2. Mix … mL of acetic acid, … mL of catalyst, and … mL of alcohol in a beaker glass. Take 5 mL of the sample as t_0. Then, add 3 drops of PP indicator and titrate with NaOH … N. Reminder that total volume for the t_0 experiment is only 1/10 of the total volume in t_1, t_2, t_3, and t_4 experiment.
3. Mix … mL of acetic acid and … mL of catalyst. Then, heat it up to …°C in a three-neck flask.
4. In a different place, heat the alcohol to a temperature of … °C in beaker glass.
5. After two reactants reach the variable temperature, mix alcohol into acetic acid solution in the three-neck flask.
6. Observe the temperature of mixture. After reaching the temperature according the variable, take 5 mL of the sample start from t_1 with a sampling time of every … minutes until the time reached … minutes.

C. Analytical Method

1. Take 5 mL of the sample, add 3 drops of PP indicator, then titrate with NaOH … N.
2. Observe the color change that occurred from colorless to weak pink. Note the amount of titrant used. Stop sampling after reaching the time of … minutes.
3. Repeat the above steps for the second variable.

HAZARD IDENTIFICATION (HI)											
A	**Mechanic**		**D**	**Environment**		**E**	**Chemicals**		**G**	**Other dangers**	
A1	Manual handling		D1	Noise		E1	Poison	√	G1	Compressed gas	
A2	Moving parts		D2	Vibration		E2	Irritant	√	G2	Ionizing radiation	
A3	Rotating parts		D3	Lighting		E3	Corrosive	√	G3	UV radiation	
A4	Cutting		D4	Moisture		E4	Carcinogenic	√	G4	Fatigue	
B	**Biology**		D5	Temperature	√	E5	Flammable	√	G5	Narrow space	
B1	Bacteria		D6	Travel hazards		E6	Explosive		G6	Overcrowded	
B2	Virus		D7	Slippery surface	√	E7	Cryogenics		G7	Thermometer	
B3	Mushroom		D8	Solid waste		**F**	**Equipment**				
C	**Electricity**		D9	Air quality	√	F1	Pressure vessels				
C1	High voltage		D10	Solitary work		F2	Hot equipment	√			
C2	Static electricity		D11	Sparks/droplets/floods	√	F3	Laser				
C3	Cable	√	D12	Powder spills	√	F4	Glass vessels				

RISK DETAILS									
HI	**Risk (after control measures)**				**Risk identification**	**Control measures to minimize risks**	**First aid measures**		
	High	**Medium**	**Low**	**Minimum**					
1. PREPARATION / INITIAL STAGE									
		√			- Reagents spill when measuring density using picnometers - Reagents spilled when weighing - Reagent spilled when inserting the titrant into the burette	Using complete personal protective equipment such as lab coats, latex gloves, and wearing shoes	- Stop the source of the spill - Stay away from reagent spills - Clean spills with proper absorbents and use full personal protective equipment - Rinse under running water if the reagent gets on the skin		
			√		Picnometers, measuring cups and pipettes fall during sampling	- Using complete personal protective equipment such as lab coats, latex gloves, and wearing shoes - Be careful when moving or moving tools so they don't get scuffed	- Away from the place where the tool fell - Cleaning tool fragments with a broom - When cleaning the fragments of the tool need to use complete personal protective equipment		
		√			The tip of the pipette breaks when taking reagents or samples	Be careful when taking the reagent so that the tip of the pipette does not come into contact with the lip of the reagent bottle	- Using full personal protective equipment - If it breaks and comes into contact with droplets, rinse immediately under running water - Removing clothes affected by droplets		
		√			- Exposed to droplets or acid spills when take from acid	- Using full personal protective equipment such	- Rinse under running water if the reagent gets on the skin		

RISK DETAILS							
HI	Risk (after control measures)				Risk identification	Control measures to minimize risks	First aid measures
	High	Medium	Low	Minimum			
					chamber - Exposed to acid droplets from a pipette that breaks the tip	as lab coats, latex gloves, as well as wearing shoes - The presence of supervision when taking reagents from the acid chamber	- Removing clothing affected by reagents
			√		Installation of the tool - The tool is dropped because it is not firmly attached - Thermometer rupture due to forcing in the installation	- Ensuring clamps firmly hold the tool - Installation of the tool should not be oblique - Installing the tool according to the available sizes	- Away from the place where the tool fell - Cleaning tool fragments with a broom - When cleaning the fragments of the tool need to use complete personal protective equipment
2. MAIN EXPERIMENTS							
				√	Electric shock when connecting an electric stove to a power source	- Make sure the power source cables and plugs are not wet - Wearing full personal protective equipment	- Turn off the source of electric current - Push the victim's body with an insulator object - Seek medical attention if there are burns
			√		The temperature of the three-neck flask and the temperature of the alcohol are too hot so that	- Controlling the flow of water in the reverse cooler - Setting the temperature of	Regulating the temperature in the device circuit with isolator protection

RISK DETAILS								
HI	Risk (after control measures)				Risk identification	Control measures to minimize risks	First aid measures
	High	Medium	Low	Minimum			
					excessive evaporation occurs	the electric stove so that it is not too high but still according to variables	
3. ANALYSIS / FINAL STAGE							
		√			- Exposed to droplets of the solution when taking samples - Exposed to drops of the solution when adding indicators - Exposed to titrant droplets when titrating	Using complete personal protective equipment such as lab coats, latex gloves, and wearing shoes	- Rinse under running water if the reagent gets on the skin - Removing clothing affected by reagents
			√		When washing tools that have been used, the tool falls and breaks because it uses laundry soap that can make it slippery	- Be careful when washing so that the tool does not slip out of the hands - Be careful when washing so that the tool does not get hit by the sink	- Away from the place where the tool fell - Cleaning tool fragments with a broom - When cleaning the fragments of the tool need to use complete personal protective equipment

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