CHAPTER I
INTRODUCTION

1.1 Background

Science and technology continue to advance, particularly in the industrial sector. In Indonesia, industries across various sectors continue to innovate and develop, including the chemical industry, both in terms of raw materials and auxiliary materials. The chemical industry uses a wide variety of raw materials and auxiliary materials, one of which is ethyl acetate, an ester compound that is widely used as a solvent in various industries. Ethyl acetate has the molecular formula $CH_3COOC_2H_5$.

Ethyl acetate is produced through an esterification reaction, in which an ester is formed from a carboxylic acid and an alcohol as the reactants. The products of an esterification reaction are an ester and water. The general equation for this reaction can be written as follows:

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

The esterification reaction is reversible and exothermic, and proceeds very slowly. However, when a mineral acid catalyst such as sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) is used, equilibrium is reached more rapidly (Jyoti & Soni, 2023). Therefore, it is necessary to study the factors affecting the reaction and conduct various experiments to determine the process variables that influence esterification.

1.2 Practical Purpose

1. To study the effect of reaction time on esterification reaction conversion.
2. To study the effect of process variables on conversion in the esterification process.
3. To study the effect of process variables on the reaction rate constant (k) in the esterification process.
4. To study the effect of process variables on the direction of equilibrium (K) in the esterification process.

1.3 Practicum Benefits

1. Students can understand the effect of reaction time on conversion in the esterification process.
2. Students can determine the effect of process variables on the conversion of the ester formed.

3. Students can learn how to observe the effect of process variables on the reaction rate constant (k) and the direction of equilibrium (K).
4. Students can conduct numerical analysis based on the experiments performed.

CHAPTER II
LITERATURE VIEW

2.1 Esters

Esters are compounds produced by the condensation reaction between carboxylic acids and alcohols. These compounds are widely used in the chemical industry. For example, adipate esters are widely used as plasticizers and organic solvents because of its high thermal stability and low volatility and toxicity (Liu & Tan, 2025).

Catalysts are used in esterification reactions to accelerate the reaction. Catalysts used in ester synthesis can be homogeneous or heterogeneous catalysts. The differences and examples of these two types of catalysts are described by Leite et al. (2025) as follows:

1. Homogenous Catalysts

   Examples of homogeneous catalysts commonly used in ester synthesis include hydrochloric, sulfuric, phosphoric, and p-toluenesulfonic acids. The advantages of homogeneous catalysts include their low cost and high conversion. However, homogeneous catalysts also have several disadvantages, including their inability to be reused, the potential to increase corrosion of equipment, and the need for additional purification steps.

2. Heterogeneous Catalysts

   Examples of heterogeneous catalysts that can be used in ester synthesis include zeolites and silica. The use of heterogeneous catalysts in ester synthesis has several advantages and disadvantages. Their advantages include easy separation from the reaction medium and recyclability. Their disadvantage is that their catalytic activity is generally lower than that of homogeneous catalysts.

2.2 Kinetics Reaction

Esterification, or the ester-forming reaction, is a reaction between a carboxylic acid and an alcohol that produces an ester and water. An example is the reaction between acetic acid and ethanol. The esterification reaction is as follows:

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$
$$A \qquad B \qquad C \qquad D$$

Chemical reaction rate equation:

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

With:

$-rA$ = reaction rate of ester formation

$[A]$ = acetic acid concentratiom $[CH_3COOH]$

$[B]$ = ethanol concentration $[C_2H_5OH]$

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

$[D]$ = water concentration $[H_2O]$

k_1 = forward reaction rate constant (product direction)

k_2 = reverse reaction rate constant (reactant direction)

t = reaction time

From a reaction kinetics perspective, the rate of ester formation increases with increasing temperature, stirring, and the use of a catalyst. This can be described by the Arrhenius equation as follows:

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

Where:

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

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, the reaction rate constant is affected by A, E_A, and T. A larger collision frequency factor (A) results in a larger reaction rate constant (k). The activation energy is affected by the use of a catalyst; a catalyst lowers the activation energy, thereby increasing the reaction rate constant (k). In addition, a higher temperature (T) also results in a higher reaction rate constant (k).

2.3 Thermodynamics Overview

From a thermodynamic perspective, whether the reaction proceeds in one direction or is reversible can be evaluated by considering the change in Gibbs energy (ΔG°). The esterification reaction between acetic acid and ethanol occurs according to the following reaction:

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

$$\Delta H^\circ_{298} = \Delta H^\circ_{f\,products} - \Delta H^\circ_{f\,reactants}$$

Known standard $\Delta H°_f$ 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

Therefore:

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

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

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

Based on the thermodynamic overview, it can also be seen that the reaction is endothermic or exothermic by considering the change in enthalpy. Based on the calculation, a negative enthalpy change (ΔH) indicates that the esterification reaction between acetic acid and ethanol is exothermic. The Gibbs energy (ΔG°) can be calculated using the following equation:

$$\Delta G°_{298} = \Delta G°_{f\,products} - \Delta G°_{f\,reactants}$$

Known standard $\Delta G°_f$ 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

Therefore:

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

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

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

From the Van't Hoff equation:

$$\Delta G°_{298} = -R.T.\ln K$$

$$\ln K = \frac{-\Delta G°_{298}}{R.T}$$

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

$$K = 6{,}5240$$

If an operating temperature of 54℃ is used in this practicum, the value of K at 54℃ can be calculated as follows:

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

$$\ln \frac{K_{313}}{6{,}5240} = -\frac{-3640\ \text{J/mol}}{8{,}314 \frac{\text{J}}{\text{mol.K}}} \left(\frac{1}{31} - \frac{1}{298}\right)$$

$$K_{327} = 5{,}7270$$

Based on the Gibbs energy calculation, the value of K at an operating temperature of 54°C is 5,7270. Therefore, the esterification reaction between acetic acid and ethanol is concluded to be reversible.

At equilibrium, with an operating temperature of 54°C and K = 5,7270, the theoretical conversion can be calculated as follows:

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

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

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

$$5{,}7270 = \frac{(X_{Ae})^2}{(1-X_{Ae})(1{,}5-X_{Ae})}$$

$$X_{Ae} = 0{,}8244$$

Therefore, at equilibrium and an operating temperature of 54°C, the theoretical conversion is 82.44% (the calculation above is only an example; practicants must adjust the reaction temperature and reactant molar ratio according to the temperature variable used in the practicum).

2.4 Reaction Mechanism

The esterification reaction is reversible, meaning that it can proceed toward ester formation or proceed in the reverse direction, decomposing the ester back into an acid and an alcohol (Jyoti & Soni, 2023). Esterification is characterized by the formation of an ester from a carboxylic acid and an alcohol (methanol or ethanol). Esterification is commonly used to process feedstocks for biodiesel production by reducing the concentration of free fatty acids (Supeno et al., 2023).

This reaction proceeds slowly at room temperature; therefore, heating and the use of a catalyst are required to accelerate the reaction rate. Catalysts used in esterification may be acidic or basic. This practicum uses acetic acid as the carboxylic acid and ethanol as the alcohol, with an acid catalyst. In the production of ethyl acetate, the esterification reaction carried out in this practicum and the acid-catalyzed mechanism of ester hydrolysis are as follows:

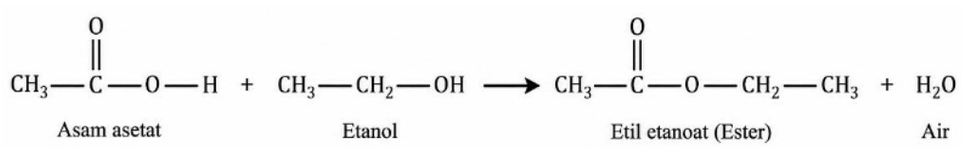
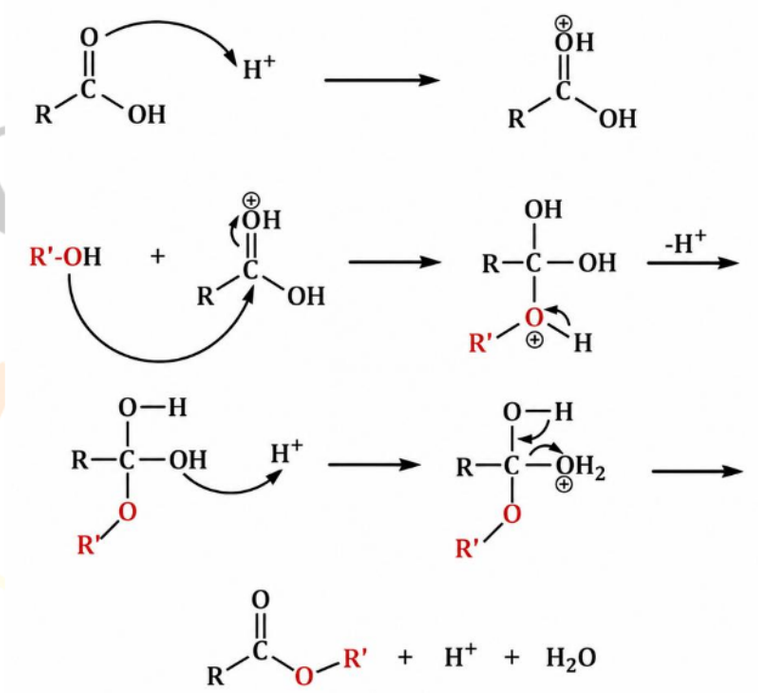


Figure 2.1 Esterification reaction

The esterification mechanism is a nucleophilic acyl substitution reaction catalyzed by an acid (usually HCl or H_2SO_4). The carbonyl group of the carboxylic acid is not sufficiently electrophilic to be attacked by the alcohol. The acid catalyst protonates the carbonyl group and activates it toward nucleophilic attack. Proton release produces a hydrated ester intermediate, followed by proton transfer.



Fugure 2.2 Esterification reaction mechanism

The acid-catalyzed esterification mechanism consists of the following steps:

1. In the first step, the carbonyl group is protonated by the acid. A proton is transferred from the acid catalyst to the carbonyl oxygen, increasing the electrophilicity of the carbonyl carbon.
2. The second step involves nucleophilic addition, in which the OH group of the alcohol attacks the protonated carbonyl carbon, forming a new C–O bond (the ester bond).
3. The third step is an equilibrium step in which the H^+ group is removed from the newly formed ester. Deprotonation occurs to form a stable C–O bond.
4. In the fourth step, one of the hydroxyl groups must be protonated because the two hydroxyl groups are identical.
5. The fift step involves breaking of the C–O bond and release of water. For this to occur, the hydroxyl group must be protonated first to improve its ability to act as a leaving group.
6. In the final step, the protonated ester releases its proton.

2.5 Influential Variables

The esterification reaction is affected by several variables, including:

1. Reaction time

   According to Lestari et al. (2022), increasing the reaction time increases the resulting conversion because contact between the substances, and therefore molecular collisions, becomes greater. However, once the process reaches equilibrium, further increases in reaction time may cause the reaction to proceed back toward the reactants, so extending the reaction time will no longer significantly affect the result (Mirzayanti et al., 2023).

2. Reactant ratio

   Stoichiometrically, the esterification reaction requires one mole of alcohol for every mole of carboxylic acid. However, because esterification is reversible, one reactant is used in excess so that the reaction is shifted toward the products, namely ester formation, in accordance with Le Chatelier's principle. Nevertheless, using an excessive amount of reactant does not always result in a significant increase in conversion because, as the system approaches equilibrium, the formation of water as a by-product can drive the reverse reaction, causing the conversion to decrease or remain relatively constant (Supeno et al., 2023).

3. Stirring

   Stoichiometrically, the esterification reaction requires one mole of alcohol for every mole of carboxylic acid. However, because esterification is reversible, one reactant is used in excess so that the reaction is shifted toward the products, namely ester formation, in accordance with Le Chatelier's principle. Nevertheless, using an excessive amount of reactant does not always result in a significant increase in conversion because, as the system approaches equilibrium, the formation of water as a by-product can drive the reverse reaction, causing the conversion to decrease or remain relatively constant (Supeno et al., 2023).

4. Temperature

   Conversion increases as the temperature increases. This is consistent with the Arrhenius equation, according to which an increase in temperature increases the reaction rate constant, causing the reaction to proceed faster. The increase in conversion with temperature will stop at a certain temperature, known as the optimum temperature, at which a further increase in temperature instead shifts the equilibrium unfavorably and does not increase conversion (Jyoti & Soni, 2023). In addition, excessively high

reaction temperatures should be avoided because increased and excessive ethanol evaporation may shift the reaction equilibrium toward the substrates (Piotrowski & Kubica, 2021).

5. Catalyst

A catalyst plays a crucial role in accelerating the esterification reaction rate. In an acid-catalyzed reaction, the catalyst activates the carbonyl group of the carboxylic acid, making it more susceptible to attack by the alcohol. This activation lowers the activation energy, allowing the ester to form much more rapidly. The catalyst is regenerated at the end of the reaction and is therefore available for the next catalytic cycle (Mannu & Mele, 2024).

CHAPTER III
PRACTICUM METHOD

3.1 Experimental Design

3.1.1 Practical Design

3.1.2 Variable

A. Fixed variable

1. Types of carboxylic acids :
2. Total volume :
3. Titration sample volume :
4. Sampling time :

B. Changed variable

3.2 Materials and Tools Used

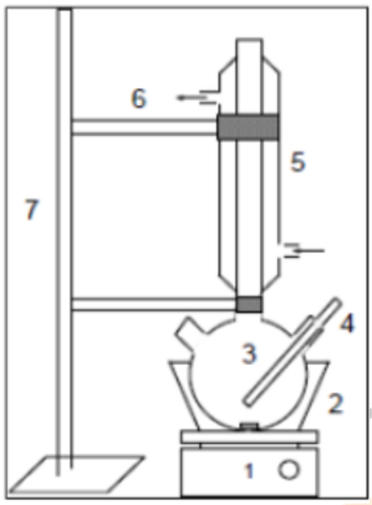
3.2.1 Materials

1. Acetic acid
2. Alcohol
3. Catalyst
4. NaOH
5. PP Indicator
6. Aquadest

3.2.2 Alat

1. Scale
2. Three-neck flask
3. Reflux condenser
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

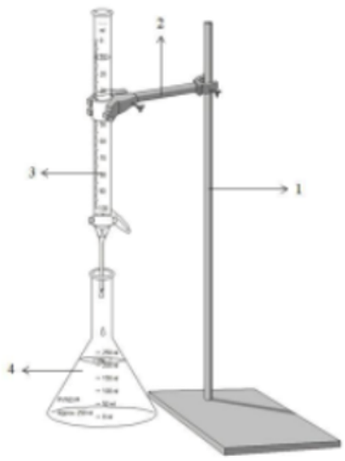
3.3 Toolkit Images



Keterangan

1. Magnetic strirrer + Heater
2. Waterbath
3. Three-neck flask
4. Thermometer
5. Reflux condenser
6. Clamp
7. Stative

Figure 3.1 Series of hydrolysis tools



Where:

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

Figure 3.2 Series of titration tools

3.4 Procedure

3.4.1 Preparation

1. Calibrate the pycnometer by weighing the empty pycnometer and recording its mass. Then fill it with distilled water, weigh it, and record its mass.
2. Measure the densities of acetic acid, the catalyst, and the alcohol using a pycnometer. Fill the pycnometer with the reagent whose density is to be determined, then weigh it and record its mass.
3. Calculate the density using the following equation:

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

4. Weigh ... grams of NaOH and dissolve it in 250 mL of distilled water. After it has dissolved, transfer the solution into the burette for use as the titrant.

3.4.2 Main Experiment

1. Assemble the tools as shown in the figures above.
2. Mix ... mL of acetic acid, ... mL of catalyst, and ... mL of alcohol in a beaker glass. Take a 5 mL sample as t0. Add 3 drops of PP indicator to the sample and titrate it using ... N NaOH. Note that the total volume in the t0 experiment is only $\frac{1}{10}$ of the total volume used for experiments t1, t2, t3, and t4.
3. Mix ... mL of acetic acid and ... mL of catalyst, then heat the mixture to ...°C in a three-neck flask.
4. In a separate container, heat ... mL of alcohol to ...°C in a beaker glass.
5. After the temperatures of the two reactants are equal, mix the two reactants in the three-neck flask.
6. Observe the temperature of the mixture. Once the temperature corresponding to the variable has been reached, take 5 mL of the sample starting at t1 at intervals of ... minutes until ... minutes have elapsed.

3.4.3 Analytical Method

1. For the analysis, take 5 mL of the sample, add 3 drops of PP indicator, and then titrate the sample with ... N NaOH.
2. Observe the color change from colorless to a faint pink color. Record the amount of titrant required. Stop sampling after ... minutes.
3. Repeat the steps above, from the preparation stage through the analysis stage, for the second variable.

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