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 et al., 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 Problem Identification

Esterification is a reaction to form an ester from a carboxylic acid and an alcohol. Generally, esterification is used in the manufacture of biodiesel. Based on the research of Kusumawati and Cahyono (2015) the main product of butanol esterification with acetic acid is butyl ethanoate with a conversion of 53% for 24 hours. In the esterification reaction there are factors that can affect the course of the reaction, such as operating temperature, reaction time, ratio of reagents, stirring, and catalyst. In this practicum, you will learn how to carry out the esterification process and determine the effect of temperature on conversion, reaction rate constants, and the direction of reaction equilibrium in the esterification process.

1.3 Practical Purpose

1. Knowing the effect of reaction time on the conversion of esterification reactions.
2. Knowing the effect of variables 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 variables on the direction of equilibrium (K) in the esterification process.

1.4 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 reaction of an ester and water. An example is the reaction between acetic acid and methanol. The esterification reactions include the following:

$$\underset{A}{CH_3COOH} + \underset{B}{CH_3OH} \leftrightarrow \underset{C}{CH_3COOCH_3} + \underset{D}{H_2O}$$

Chemical reaction rate equation:

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

With :

$-rA$	=	reaction rate of formation ester
[A]	=	acetic acid concentration [CH_3COOH]
[B]	=	methanol concentration [CH_3OH]
[C]	=	methyl acetate concentration [CH_3COOCH_3]
[D]	=	water concentration [H_2O]
k_1	=	reaction rate constant to the right (product direction)
k_2	=	reaction rate constant to the left (direction reactants)
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.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, 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 increase. The higher the temperature (T), the value of k also getting bigger. From the results of research conducted by Kirbaskar et al. (2001) for the esterification reaction of acetic acid with methanol using an acid catalyst with ion exchange resin, it was found that for the reaction towards the formation of the product (k_1) has a value of E_A = 104129 kJ/kmol and A = $2.6\times10^{14}(m^3)^2$ $kmol^{-2}s^{-1}$.

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 (ΔG°). The esterification reaction between acetic acid and methanol occurs according to the following reaction:

$$CH_3COOH + CH_3OH \leftrightarrow CH_3COOCH_3 + H_2O$$

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

1. Known standard H°f data (Smith et al., 2001)

$\Delta H°_{f298}$ CH_3COOH = -484500 J/mol

$\Delta H°_{f298}$ CH_3OH = -238600 J/mol

$\Delta H°_{f298}$ CH_3COOCH_3 = -445890 J/mol

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

So :

$$\Delta H°_{298} = (\Delta H°_{f298}\ C + H°_{f298}\ D) - (\Delta H°_{f298}\ A + H°_{f298}\ B)$$
$$= (-445890 \text{ J/mol} - 285830 \text{ J/mol}) - (-484500 \text{ J/mol} - 238600 \text{ J/mol})$$
$$= -8620 \text{ J/mol}$$

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 methanol is exothermic.

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

$\Delta G°_{f298}$ CH_3COOH = -389900 J/mol

$\Delta G°_{f298}$ CH_3OH = -166270 J/mol

$\Delta G°_{f298}$ CH_3COOCH_3 = -324200 J/mol

$\Delta G°_{f298}$ H_2O = -237129 J/mol

So :

$$\Delta G°_{f298} = (\Delta G°_{f298}\ C + G°_{f298}\ D) - (\Delta G°_{f298}\ A + G°_{f298}\ B)$$
$$= (-324200 \text{ J/mol} - 237129 \text{ J/mol}) - (-389900 \text{ J/mol} - 166270 \text{ J/mol})$$
$$= -5159 \text{ J/mol}$$

From the van't Hoff equation:

$$\Delta G°_{298} = -R.T.\ln K$$

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

$$\ln K = -\frac{(-5159)\,J/mol}{8{,}314\frac{J}{mol.K}\,(298K)}$$

$$K = 8{,}022$$

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

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

$$\ln \frac{K_{327}}{8{,}022} = -\frac{(-\,8620\,)\frac{J}{mol}}{8{,}314\frac{J}{mol\,K}}\left(\frac{1}{327} - \frac{1}{298}\right)K$$

$$K_{313} = 5{,}892$$

From the Gibbs energy calculation, the K value at an operating temperature of 54°C is obtained and a value of 5,892 is obtained. So it can be concluded that the esterification reaction of acetic acid with methanol is a reversible reaction.

Calculating theoretical conversion value.

On operating temperature of 54°C the value of K = 5.892 is obtained.

At equilibrium:

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

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

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

$$6{,}7987 = \frac{(X_{Ae})^2}{(1-X_{Ae})(1{,}5-X_{Ae})}$$

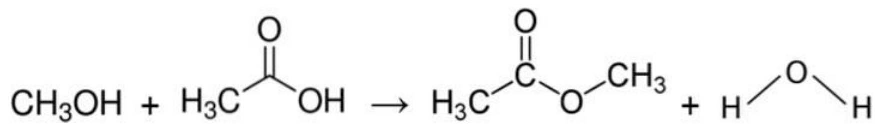
$$X_{Ae} = 0{,}8273$$

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 and the reaction is reversible (Supardjan, 2004). 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:



Methanol Acetic Acid Methyl Acetate Water

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.

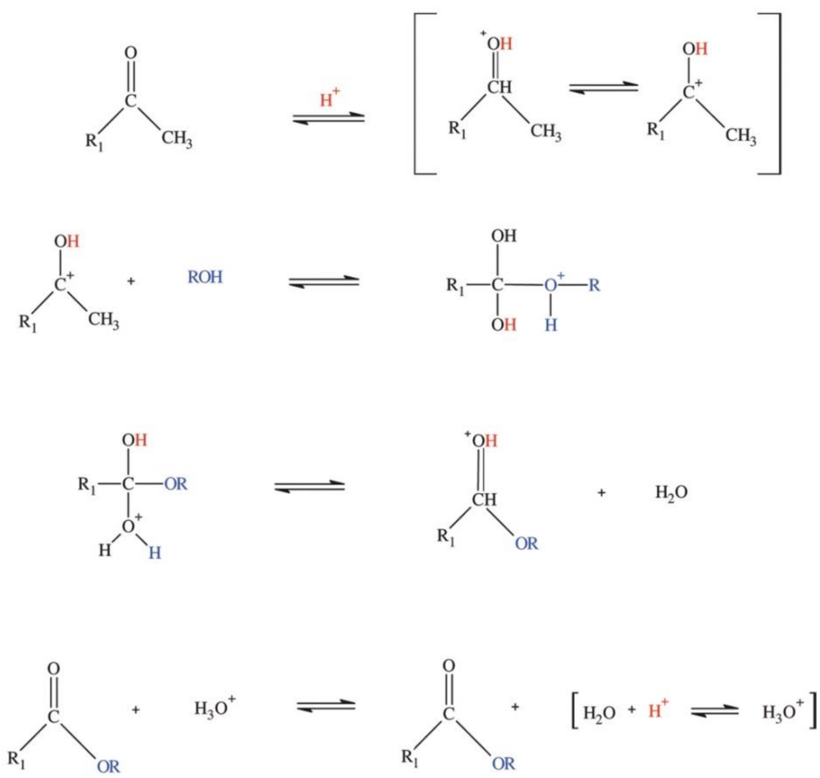


Figure 2.2 Mechanism of esterification reaction

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 include:

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 reagents

    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 acids :

Total volume :

Titration sample volume :

Sampling time :

B. Variable changed

3.2 Materials and Tools Used

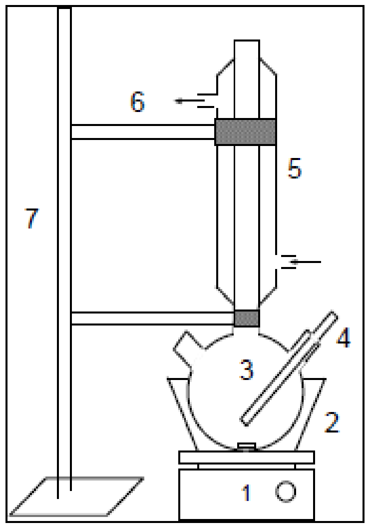
3.2.1 Ingredient

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

3.2.2 Tool

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

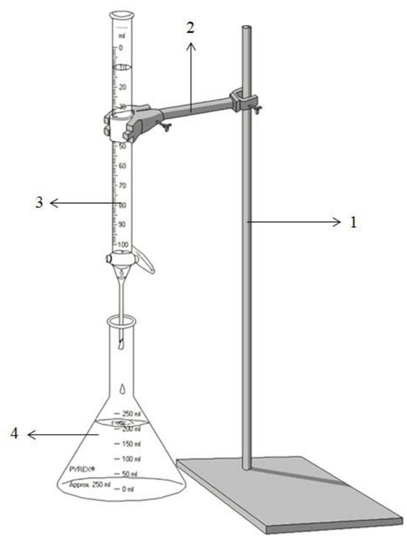
3.3 Toolkit Images



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

1. \

Figure 3.3 Series of titration tools

3.4 Procedure

1. Assemble the tools as in the picture.
2. Mix acetic acid … mL, catalyst … mL, and alcohol … mL in a beaker glass. Take 5 mL of the sample, add 3 drops of PP indicator, then titrate using NaOH … N. It should be noted that the total volume for the t_0 experiment was only 1/10 of the total volume in experiments t_1 t_2 t_3, and t_4.
3. Mix acetic acid … mL, and catalyst … mL. 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 a beaker glass.
5. After the temperature of the two reactants is the same, mix the two reactants

into the three-neck flask.

6. Observe the temperature of the mixture. After reaching the temperature according to the variable, take 5 mL of the sample starting from t_1 with a sampling time of every … minutes until the time reached … minutes.
7. The analytical method, take 5 mL of the sample, add 3 drops of PP indicator, then titrate using NaOH … N. Observe the color change that occurred, from colorless to pink almost disappeared. Note the need for titrant. Stops sampling after reaching the time of … minutes.
8. Repeat the above steps for the second variable.

BIBLIOGRAPHY

Almeida, E. L., Andrade, C. M. G., & dos Santos, O. A. (2018). Production of biodiesel via catalytic processes: A brief review. *International Journal of Chemical Reactor Engineering*, *16*(5).

Kastratović, V., & Bigović, M. (2018). Esterification of stearic acid with lower monohydroxylic alcohols. *Chemical Industry and Chemical Engineering Quarterly*, *24*(3), 283-291.

Kusmiyati. (2008). Reaksi Katalitis Esterifikasi Asam Oleat dan Metanol Menjadi Biodiesel dengan Metode Distilasi Reaktif. *Reaktor, 12*(2), 78-82. https://doi.org/10.14710/reaktor.12.2.78-82

Levenspiel. O. (1999). *Chemical reaction Engineering*. (3rd ed.). Mc. Graw Hill Book Kogakusha Ltd, Tokyo.

Nurhayati, N., Anita, S., Amri, T. A., & Linggawati, A. (2017). Esterification of Crude Palm Oil Using H 2 SO 4 and Transesterification Using CaO Catalyst Derived from Anadara granosa. *Indonesian Journal of Chemistry*, *17*(2), 309-315.

Nuryoto, Amaliah A.R., Puspitasari A., & Ramadhan A. D. (2020). Study of Esterification Reaction between Ethanol and Acetic Acid Using Homogeneous and Heterogeneous Catalyst. World Chemical Engineering Journal Vol.4, No.2, (2020), pp. 51 – 55

Nuryoto, Sulistryo, H., Suprihastuti, Rahayu, S. & Sutijan. (2011). Kinetika Reaksi Esterifikasi Gliserol dengan Asam Asetat Menggunakan Katalisator Indion 225. *Jurnal Rekayasa Proses, 5*(2),35-39. Na. https://doi.org/10.22146/jrekpros.1897

Panchal, B., Chang, T., Kang, Y., Qin, S., Zhao, Q., Wang, J., ... & Sun, Y. (2020). Synthesis of polymer based catalyst: Optimization and kinetics modeling of the transesterification of Pistacia chinensis oil with diethyl carbonate using acidic ionic liquids. *Fuel*, *276*, 118121.

Smith, J.M., Ness, H. C. V., & Abbott, M. M. (2001). *Introduction to Chemical Engineering Thermodynamics*. (6th ed.). Mc Graw Hill.

Supardjan. (2004). Sintesis Diasetil Heksagamavunon-1 dengan Katalis Basa. *Pharmacon,5*(2),48-55.

Susanti, M. M. (2019). Sintesis Senyawa Etil Laurat Menggunakan Variasi Volume Katalis Asam Sulfat Pekat. *Jurnal Labora Medika, 3*(1), 1-9.

Wendi, W. (2014). Effect of Reaction Temperature and Catalyst Concentration. In *Sriwijaya International Seminar on Energy-Environmental Science and Technology* (Vol. 1, No. 1, pp. 32-37).