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Reaction Kinetics of Acetic Acid with Ethanol to Ethyl Acetate with Sulfuric Acid Catalyst

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ABSTRACT: Ethyl acetate is an ester of ethanol and acetic acid. This compound is a colorless liquid with a characteristic odor. Ethyl acetate is widely used as a solvent because of its high solubility. The manufacture of ethyl acetate (ethyl ester) is referred to as the esterification process. This esterification reaction is an exothermic reaction, is reversible and generally runs very slowly so it requires a catalyst to obtain maximum ester. Domestic demand for ethyl acetate is increasing, while production in Indonesia is still lacking. Reactor design requires a reaction mechanism and kinetic data in the form of reaction rate equations and reaction rate constants. This study aims to determine the kinetics of the etherification of acetic acid presented in the form of the reaction rate equation, the value of the reaction rate constant, and the reaction equilibrium constant. In addition, this research also studied how the influence of sulfuric acid catalyst on the reaction rate constant and the reaction balance. The esterification reaction was carried out in a batch reactor. 99% acetic acid and H_2SO_4 catalyst whose concentrations are varied, are mixed in a reactor equipped with a magnetic stirrer which is operated at 400 rpm, then 96% ethanol is poured with a volume ratio of 1:1 to acetic acid, 5 mL of sample is taken to analyze the remaining acid after The reaction takes place, every certain time interval a sample is taken to be analyzed until an equilibrium point is obtained. From the results of this study it can be concluded that the esterification reaction of acetic acid with ethanol to produce ethyl acetate is a second order reaction with the reaction rate equation $(-r_A) = k_1C_AC_B - k_2C_CC_D$. By using a reaction temperature of 34ºC and a stirring speed of 400 rpm, the best conditions were obtained using a catalyst of 5.3% by volume, with the reaction rate constant to the right (k_1) being 0.014 L/(gmol min), the value of the equilibrium constant ($K=k_1/k_2$) is 5.51 and the balance conversion is 77%.

KEY WORD: Catalyst, Esterification, Ethyl acetate

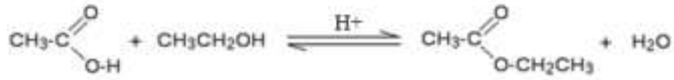
1. INTRODUCTION

Major industries that are growing rapidly in Indonesia today are the cosmetic, paint, detergent, glue, ink, thinner, poly-vinyl chloride (PVC) film, and organic chemical industries. These industries in the manufacture of their products, require large amounts of solvents. The solvent most often used is ethyl acetate ($CH_3COOC_2H_5$). Ethyl acetate is a colorless liquid with a molecular weight of 88.10 g/mol. Ethyl acetate is easily soluble in water and organic solvents, such as alcohol, acetone, ether and chloroform (Dutia, 2004). Ethyl acetate is a semi-polar solvent with low toxicity, so it is expected to attract polar and non-polar compounds. (Putri, W. S., et al, 2013). Ethyl acetate is commonly used as a flavor enhancer (Azura, S.L., and Sutri, R., 2015). Ethyl acetate can be used as a solvent in the extraction of pharmaceutical and food products (Konakom et al., 2010).

Ethyl acetate is made by reacting acetic acid with alcohol to produce ethyl acetate and water which is called the Fischer esterification reaction. This esterification reaction is an exothermic reaction, is reversible and generally runs very slowly so it requires a catalyst to obtain maximum ester. (Suleman, N., 2017). Esterification is the reaction of converting a carboxylic acid and an alcohol into an ester using an acid catalyst. (Widyawati, Yeti. 2007). Domestic demand for ethyl acetate is increasing, while domestic production has not met demand, a new ethyl acetate plant is needed to meet domestic demand for ethyl acetate.

The Fischer esterification reaction of acetic acid and ethanol is usually accompanied by an acid catalyst such as sulfuric acid, producing orange-scented ethyl acetate (synthetic flavour). (Fatimah, I., & Julianto, T. S., 2004). The esterification reaction is a reversible reaction, that is, a reaction that can be reversed. Reaction equilibrium will be reached when the rate of reaction towards the products is equal to the rate of reaction towards the reactants. At that time the concentration of reactants and reaction products remained relatively constant. (Setyawardani, D. A., et al., 2013). The equation for the esterification reaction of acetic acid with ethanol to form ethyl acetate and water can be written as follows (Kirk, R. E., and R.F. Othmer, 1951):

CH_3COOH + CH_3CH_2OH ⇌ $CH_3COOCH_2CH_3$ + H_2O



Acetic acid Ethanol Ethyl Acetate Water

The reversible chemical reaction velocity equation model can be written as follows: (Pasaribu, A. A., and Rustamaji, H., 2016).

$$r_A = -\frac{dC_A}{dt} = k_1\, C_A C_B - k_2 C_C\, C_D$$

In terms of the reaction kinetics, the speed of the ester formation reaction will increase with increasing temperature, stirring and adding a catalyst. This can be explained by the Arrenius equation, namely (Levenspiel and Octaf, 1999):

$$k = Ae^{(-E/RT)}$$

k = reaction rate constant
A = collision frequency factor
T = Temperature
Ae = Activation Energy
R = gas constant constant

Based on the Arrhenius equation, it can be seen that the reaction rate constant is influenced by the values of A, E, and T. Where the greater the collision factor (A), the greater the reaction rate constant, the greater the stirring speed, the greater the possibility of collisions. The value of the activation energy (E) is affected by the use of a catalyst, the presence of a catalyst will reduce the activation energy so that the value of k is greater. Increasing the concentration of the catalyst will further lower the activation energy, thereby increasing the number of activated molecules which results in an increase in the reaction rate. (Purnami, P., et al., (2015).

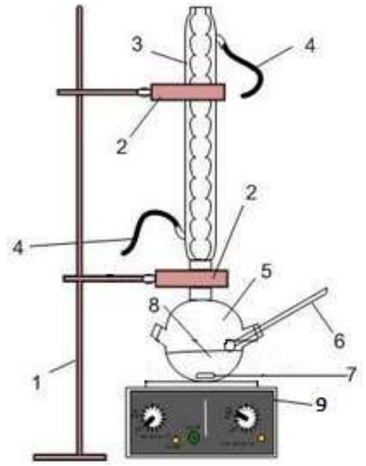
The higher the temperature (T), the greater the value of k. Based on a thermodynamic review, an increase in temperature can shift the equilibrium to the left (towards the formation of reactants) because the esterification reaction between acetic acid and ethanol is exothermic and reversible. (Smith,J.M.,1981). The choice of using sulfuric acid (H_2SO_4) as a catalyst in the esterification reaction is due to several factors, including (Satriadi, H., 2015):

1. Sulfuric acid besides being acidic is also a strong oxidizing agent.
2. Sulfuric acid is soluble in water at all concentrations
3. The reaction between sulfuric acid and water is a strongly exothermic reaction
4. If concentrated sulfuric acid is added to water, it is capable of boiling
5. Because of its affinity for water, sulfuric acid can remove most of the moisture and wet gases, such as moist air.
6. The concentration of H+ ions affects the reaction rate.
7. Concentrated sulfuric acid is able to bind water (hygroscopic), so for an equilibrium reaction that produces water it can shift the direction of the reaction to the right (towards the product).

From the factors above, it can be concluded that the addition of sulfuric acid as a catalyst to speed up the reaction rate because the reaction between sulfuric acid and water (the esterification process) to produce ethyl acetate and water is a strong exothermic reaction. Water added with concentrated sulfuric acid will be able to boil, so the reaction temperature will be high. The higher the reaction temperature, the more molecules that have energy greater than or equal to the activation energy, so the reaction is faster. (Sukardjo, 1997).

A catalyst is added so that the reaction takes place with a lower activation energy so that the value of the reaction rate constant (k) will be greater, so that the reaction speed will also be greater. (Megawati, E., et al., 2022). In addition, because concentrated sulfuric acid is able to bind water (hygroscopic), then for a balanced esterification reaction that produces water, concentrated sulfuric acid can shift the reaction direction to the right (towards the product), so that the resulting product becomes more. (Sukardjo, 1997)

This study aims to determine the kinetics of the etherification of acetic acid by presenting the reaction rate equation, the value of the reaction rate constant, and the reaction equilibrium constant. In addition, this study also studied how the influence of sulfuric acid catalyst on the reaction rate constant and the reaction balance. In this study, 99% acetic acid, 96% ethanol and 98% sulfuric acid were used as catalysts. The esterification process begins with assembling the experimental apparatus, then 99% acetic acid and 98% H2SO4 catalyst with variations (2.7%; 4.0%; 5.3%; 6.7% v/v to acetic acid), mixed in three neck flask. Then the magnetic stirrer was run at 400 rpm, then 96% ethanol was poured with a volume ratio of 1:1 to acetic acid into a three neck flask. Then 5 mL of sample was taken to analyze the remaining acid starting from the beginning of the reaction t = 0 with a time of taking each certain time interval until the equilibrium point was obtained. The equipment used for the esterification process is as follows (Figure 1).



Information:
1. Static
2. Clamps
3. Cooling back
4. Cooling water line
5. Three neck pumpkin
6. Thermometer
7. Magnetic stirrer
8. Ethyl acetate solution
9 Electric stoves

Figure 1. A series of esterification devices

2. RESULTS AND DISCUSSION

Determine the Reaction Speed Equation

The equation for the esterification reaction of acetic acid with ethanol to become ethyl acetate and water is a back and forth reaction which can be written as follows:

CH_3COOH + CH_3CH_2OH $\rightleftarrows$ $CH_3COOCH_2CH_3$ + H_2O

Acetic acid Ethanol Ethyl Acetate Water

The reaction rate equation can be expressed by (Smith, J.M., 1981):

reaction velocity to the right: $r_1 = k_1 C_A^p C_B^q$

reaction velocity to the left: $r_2 = k_2 C_C^r C_D^s$

The values of k_1, k_2, p, q, r, and s can be obtained experimentally by reacting acetic acid with ethanol and observing changes in the concentration of acetic acid at each time until equilibrium is reached.

Table 1. Relationship between time (t) and acetic acid concentration

t (minute)	C_A (gmol/L)			t (minute)	C_A (gmol/L)
	2,67 %	4%	5,3 %		6,67%
0	8,1414	8,1414	8,1414	0	8,1414
4	6,031	6,263	3,740	3	4,492
8	5,045	4,755	2,870	6	3,323
12	4,436	3,740	2,493	9	2,892
16	4,030	3,247	2,203	12	2,646
20	3,740	3,015	2,116	15	2,400
24	3,450	2,812	2,000	18	2,277
28	3,334	2,725	1,971	21	2,277
32	3,160	2,638	1,942	24	2,154
36	3,044	2,522	1,884	27	2,092
40	2,899	2,464	1,855	30	1,969
44	2,870	2,377	1,826	33	1,969
48	2,754	2,391	1,797	36	1,969
52	2,638	2,290	1,797	39	1,969
56	2,638	2,261	1,797	-	-
60	2,638	2,203	1,797	-	-
64	2,638	2,174	-	-	-
68	-	2,116	-	-	-
72	-	2,116	-	-	-

From the analysis results obtained a relationship between time (t) and the concentration of acetic acid (C_A) at various variations of the addition of catalyst (% v/v to acetic acid), as shown in table 1 is the relationship between time (t) and the concentration of acetic acid at various variations of catalyst addition (% v/v to acetic acid) with C_{A0} = 8.1414 gmol/L; C_{B0} = 10.2972 gmol/L; T average = 34°C; stirring speed = 400 rpm.

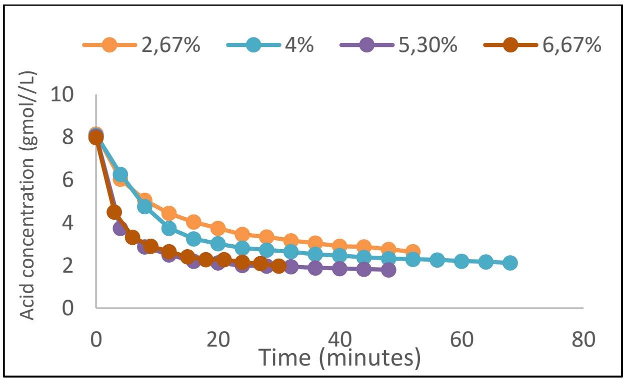


Figure 2. Graph of the relationship between time (t) and the concentration of acetic acid (CA) at various variations in the addition of the amount of catalyst

Table 1 and Figure 2 show that the greater the addition of catalyst, the smaller the concentration of acetic acid at the same time. This shows that the reaction speed is getting bigger. The form of the reaction equation can be determined by the following steps:

a. Predict the reaction order

The first step predicts a rightward reaction order of 2 (one for acetic acid and one for ethanol or p = 1 and q = 1) and a leftward reaction order of 2 (one for ethyl acetate and one for water or r = 1 and s = 1) , so the chemical reaction rate equation is as follows:

$$r_A = -\frac{dC_A}{dt} = k_1\, C_A C_B - k_2 C_C C_D$$

b. Determine the linear equation of the mass balance. In the literature review, the mass balance has been described for the second order reaction, and the following equation is obtained:

$$-(k_1 C_A(C_{B0} - (C_{A0} - C_A)) - k_2(C_{A0} - C_A)(C_{A0} - C_A)) = \frac{dC_A}{dt}$$

The above equation is integrated by entering data from table 1, the following equation is obtained:

$$-(\frac{1}{20{,}688} ln \frac{C_A - 2{,}6388}{C_{A0} - 2{,}6388} + \frac{1}{20{,}688} ln \frac{C_A + 18{,}0292}{C_{A0} + 18{,}0292}) = k_1 t$$

The equation above is a linear equation y = kt, with:

$$y = -(\frac{1}{20{,}688} ln \frac{C_A - 2{,}6388}{C_{A0} - 2{,}6388} + \frac{1}{20{,}688} ln \frac{C_A + 18{,}0292}{C_{A0} + 18{,}0292})$$

From the equation above, a table 2 can be made of the relationship between t (time) and y for each addition of the catalyst.

Table 2. Relationship between t and y values for each addition of catalyst (% v/v to acetic acid)

t (minute)	Y 2,67 %	4%	5,3%	t (minute)	Y 6,67 %
4	0,0193	0,0207	0,0875	3	0,0572
8	0,0339	0,0491	0,1404	6	0,1047
12	0,0467	0,0823	0,1811	9	0,1357
16	0,0582	0,1082	0,2335	12	0,1616
20	0,0689	0,1251	0,2573	15	0,2000
24	0,0830	0,1443	0,3025	18	0,2290
28	0,0902	0,1544	0,3180	21	0,2290
32	0,1037	0,1661	0,3364	24	0,2736
36	0,1156	0,1854	0,3881	27	0,3092
40	0,1366	0,1973	0,4294	-	-
44	0,1423	0,2196	0,5001	-	-
48	0,1755	0,2393	-	-	-
52	-	0,2513	-	-	-
56	-	0,2657	-	-	-
60	-	0,3059	-	-	-
64	-	0,3380	-	-	-

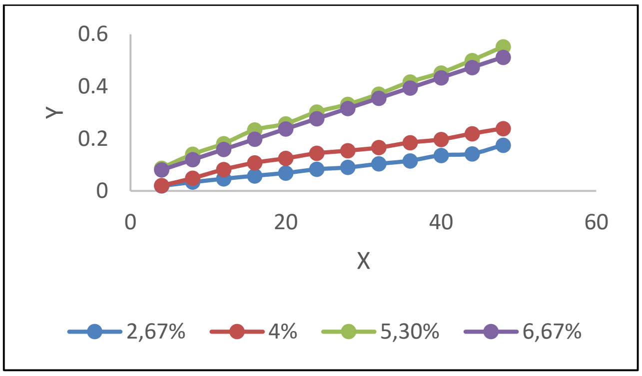


Figure 3. Graph of the x and y relationship for various catalyst amounts

Figure 3 shows that the x and y relationship for various catalyst additions is close to linear. It can be concluded that the esterification reaction of acetic acid with ethanol to ethyl acetate is a 2nd order reaction to the right and 2nd order to the left, namely $r_A = k_1C_AC_B - k_2C_CC_D$.

The value of k (reaction rate constant) can be calculated by the Least Square method. The value of k_1 at various catalyst additions can be seen in table 3

Table 3. The effect of adding catalyst volume to the reaction rate constant (k_1)

Catalyst addition (%)	Reaction rate constant to the right (L/(gmol.minute))
2,67	0,0033
4	0,0046
5,3	0,0101
6,67	0,0098

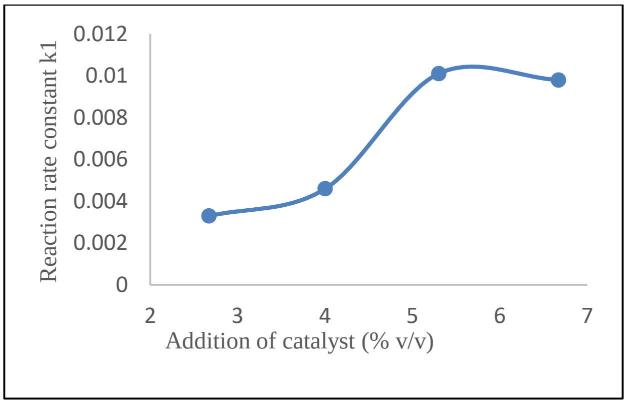


Figure 4. Graph of the relationship between the addition of catalyst and the reaction rate constant to the right.

In Figure 4 it can be seen that the more catalyst volume added, the greater the reaction rate constant. This is because the addition of a catalyst will lower the activation energy needed to react so that the reaction rate constant will be greater. However, with the addition of the amount of catalyst above the 5.3% constant, the reaction rate to the right decreased. This is due to the fact that the greater the speed of the reaction to the right will produce more water in a short time, while the increase in the ability of H2SO4 to absorb water is not significant, so that the reaction shift to the right decreases and shifts to the left. This can also be seen from the decrease in the constant value of the decreasing reaction balance shown in Figure 5. Activation energy is the minimum energy that must be met for a reaction to occur. The relationship between the reaction rate constant (k) and the activation energy (E) can be seen by the Arrhenius equation (Levenspiel, 1972):

$k = A.e^{(-E/RT)}$

with:

k = reaction rate constant
A = collision frequency factor
E = activation energy
R = universal gas constant
T = reaction temperature

At a certain collision frequency (A), universal gas constant (R), and reaction temperature (T), the smaller the value of the activation energy (E), the value of k will increase.

An increase in the concentration of the catalyst will further lower the activation energy, thus increasing the number of activated molecules which results in an increase in the reaction rate, but the water that is formed is faster and can reduce the shift of the reaction to the right.

The effect of the amount of catalyst on the equilibrium constant can be seen in Table 4 and Figure 5 which is obtained through the calculation results from the following equation:

$$Xe = \frac{C_{ce}C_{De}}{C_{Ae}C_{Be}}$$

C_{Ae} = concentration of acetic acid at equilibrium (gmol/L)
C_{Be} = ethanol concentration at equilibrium (gmol/L)
C_{Ce} = concentration of ethyl acetate at equilibrium (gmol/L)
C_{Ce} = water concentration at equilibrium (gmol/L)

Table 4. The relationship between the addition of catalyst (% v/v to acetic acid) with the equilibrium constant (K)

Addition of catalyst (%)	Equilibrium constant (K)
2,67	2,393211
4	3,955487
5,3	5,513133
6,67	4,497816

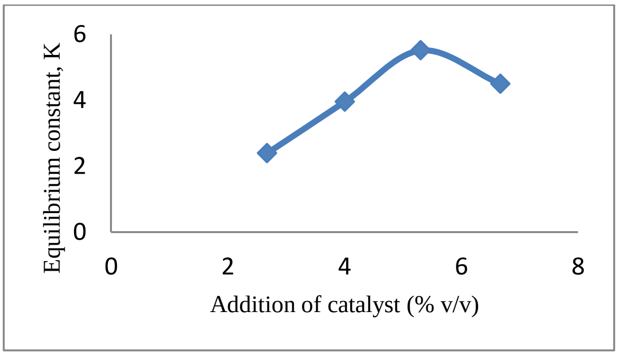


Figure 5. Graph of the relationship between the addition of catalyst and the equilibrium constant.

In Figure 5 it can be seen that the greater the amount of H_2SO_4, the greater the balance constant, but if it is too large, the equilibrium constant drops.

As the equilibrium constant changes, it will affect the change in the equilibrium conversion. From the data table 1 it can be calculated the equilibrium conversion (Xe) for each addition of the catalyst with the following calculation:

$$Xe = \frac{C_{A0}-C_{Ae}}{C_{A0}}$$

C_{A0} = initial concentration of acetic acid (gmol/L)
C_{Ae} = concentration of acetic acid at equilibrium (gmol/L)

The relationship between the addition of catalyst (% v/v to acetic acid) and the equilibrium conversion (Xe) can be seen in Table 5 and Figure 6.

Table 5. Effect of adding catalyst volume to equilibrium conversion (Xe).

Catalyst addition (%)	Equilibrium conversion (Xe)
2,67	0,675879
4	0,73828
5,3	0,776264
6,67	0,753319

In Figure 6 it can be seen that the more catalyst added the equilibrium conversion will be greater until the addition of 5.3% catalyst then drops to the addition of 6.67% catalyst, because in these conditions the reaction shifts to the left

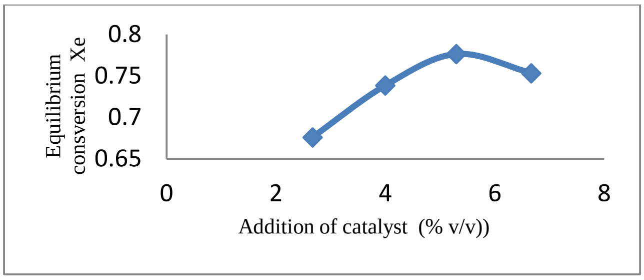


Figure 6. Graph of the relationship between the additions of catalyst to the equilibrium conversion.

3. CONCLUSION

The esterification reaction of acetic acid with ethanol to form ethyl acetate is a balanced reaction with the reaction rate of order 2 to the right and order 2 to the left with the reaction rate equation $r_A = k_1C_AC_B - k_2C_CC_D$. where k_1 = reaction rate constant to the right, C_A = acetic acid concentration, C_B = ethanol concentration, k_2 = reaction rate constant to the left, C_C = ethyl acetate concentration and C_D = water concentration. The addition of sulfuric acid catalyst affects the reaction rate, the more volume of catalyst added, the value of the reaction rate constant to the right (k_1) and the reaction speed to the left (k_2), is greater, but when the catalyst is added more than a certain amount there is a decrease in the reaction rate to the right and the constant balance decreases or the reaction shift to the right decreases. By using a reaction temperature of 34°C and a stirring speed of 400 rpm, the best conditions were obtained by using a catalyst of 5.3% by volume of acetic acid, with the reaction rate constant to the right (k_1) being 0.014 L/(gmol min), the value of the equilibrium constant ($K=k_1/k_2$) is 5.51 with a balance conversion of 77%.

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