

CHAPTER 1

INTRODUCTION

1.1 Background

The stirred tank reactor is the most common reactor in the chemical industry. In large-scale industries, stirred tank flow reactors are more often applied because of their adjustable operating capacity. The performance of the stirred flow reactor needs to be studied to determine the characteristics of the fluid flow, the reactions that occur in the optimization of the operation of the reactor.

The operation of the stirred tank flow reactor includes three stages, namely filling the reactor with high overflow, continuous conditions, and continuous steady state. Evaluation of operating variables is very easy to do at steady state conditions.

Mathematical modeling is needed to facilitate the analysis of problems that arise in the operation of the stirred tank flow reactor. The proposed mathematical model is tested for accuracy by comparing it with experimental data. The proposed mathematical model is solved by means of analysis if the equation is easy to solve. However, for complex reactions, a complex mathematical model will also be obtained. Numerical method is highly recommended to obtain the value of k , mass transfer constant, and reaction order which are adjustable parameters.

1.2 Problem Formulation

The Ideal Continuous Flow Reactor / Stirred Tank Flow Reactor is a place where a chemical reaction of formation or decomposition occurs, where the mass flow enters or exits continuously (continuously) (Rosadi, 2000). In this practicum, the ideal continuous flow reactor will be studied to determine the value of the reaction order, reaction constants and the effect of NaOH concentration and compare the calculation of the mathematical model of Ethyl acetate saponification with NaOH in an Ideal Continuous Flow Reactor.

1.3 Purpose

1. Determine the value of the reaction order for ethyl acetate saponification with NaOH.
2. Calculate the value of the reaction constant (k) for saponification of Ethyl acetate with NaOH.

3. Knowing the effect of variables on the reaction constant (k) of saponification of ethyl acetate with NaOH.
4. Comparing the experimental results with the calculation of the mathematical model of the runge kutta method for the saponification reaction in an ideal continuous flow reactor.

1.4 Benefits

1. Students can determine the order of the reaction for saponification of Ethyl acetate with NaOH.
2. Students can calculate the value of the reaction constant (k) for saponification of Ethyl acetate with NaOH.
3. Students are able to determine the effect of variables on the reaction constant (k) of saponification of ethyl acetate with NaOH.
4. Students are able to compare the experimental results with the calculation of the mathematical model of the runge kutta method for the saponification reaction in an ideal continuous flow reactor.

CHAPTER II

LITERATURE REVIEW

2.1 Batch Reactor

Material balance in reactor simultaneously

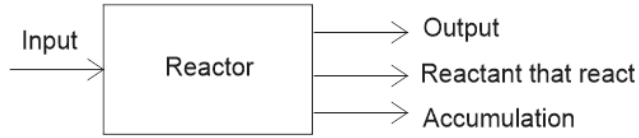


Figure 2.1 Part of the mass balance of a system

Input = 0

Output = 0

Reactants that react = $(-r_A)$

Input = output + reactants react + accumulation

$$0 = 0 + v(-r_A) + \frac{dN_A}{dt} \quad \dots(1)$$

$$0 = V_i(-r_A) + \frac{d[N_{A0}(1-X_A)]}{dt} \quad \dots(2)$$

$$0 = V_i(-r_A) - \frac{N_{A0}dX_A}{dt} \quad \dots(3)$$

$$dt = \frac{N_{A0}}{V_i(-r_A)} dX_A \quad \dots(4)$$

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{V_i(-r_A)} \quad \dots(5)$$

At constant volume

$$C_A = C_{A0}(1-X_A)$$

$$dC_A = -C_{A0} \cdot dX_A \quad \dots(6)$$

Eq. (6) goes to the Eq. (5) obtained:

$$t = C_{A0} \int_0^{X_A} \frac{dN_A}{-r_A} = - \int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A} \quad \dots(7)$$

2.2 Continuous Flow Ideal Reactor/Stirred Flow Tank Reactor (CSTR)

The stages that occur in the CSTR reactor are divided into 3 process stages, namely:

a. The first stage

The first stage starts at $t=0$ until overflow

From the law of conservation of mass

Accumulation = input – output

$$\rho \frac{dV}{dt} = \rho \cdot Fo - 0 \quad \dots(8)$$

$$dV = Fo \cdot dt, \text{ at } t = 0 \rightarrow V = 0$$

Since the density of the flow rate is considered constant, its volume is only a function of time.

$$V = F_o \cdot t \quad \dots(9)$$

Meanwhile, from the component balance sheet:

Accumulation = input – output – rate of consumption due to reaction

$$\frac{d}{dt}(V \cdot C) = F_o \cdot C_o - 0 - V(-r_A) \quad \dots(10)$$

In this case :

V = Volume material in reactor (l)

C = Molar concentration of reactants in the reactor (mol/l)

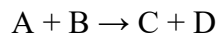
F_o = Incoming reactant flow rate (l/mol)

C_o = Molar concentration of reactants in feed (mol/l)

t = Time of reaction occurred (minutes)

-r_A = Reaction rate (mol/min)

The reactions that occur are:



-r_A = k · C_AC_B, since C_A = C_B, then

$$-r_A = kC_A^2 = kC^2 \quad \dots(11)$$

Eq. (11) → Eq. (10)

$$\begin{aligned} \frac{d(V \cdot C)}{dt} &= F_o \cdot C_o - V \cdot k \cdot C^2 \\ V \frac{dC}{dt} + C \frac{dV}{dt} &= F_o \cdot C_o - V \cdot k \cdot C^2 \end{aligned} \quad \dots(12)$$

Eq. (9) → Eq. (12)

$$F_o \cdot t \cdot \frac{dC}{dt} + C \cdot F_o = F_o \cdot C_o - F_o \cdot t \cdot k \cdot C^2 \quad \dots(13)$$

$$\frac{dC}{dt} = \frac{C_o}{t} - \frac{C}{t} - k \cdot C^2 \quad \dots(14)$$

By using the boundary condition at t=0, C=C_o and substitution $U = e^{k \int C \cdot dt}$, then Eq. (14) becomes:

$$t^2 \frac{d^2U}{dt^2} + t \frac{dU}{dt} - k \cdot U \cdot C_o \cdot t = 0 \quad \dots(15)$$

Eq. (15) is converted into a Bessel Function by substitution z=t0,5, to become:

$$z^2 \frac{d^2U}{dt^2} + z \frac{dU}{dt} - 4 \cdot k \cdot U \cdot C_o \cdot z^2 = 0 \quad \dots(16)$$

Eq. (16) is a modification of the Bessel Equation which has the following general form:

$$\begin{aligned} x^2 \frac{d^2y}{dx^2} + x(a + 2bx^r) \frac{dy}{dx} + [c + dx^{2s} - b(1 - a - r)x \cdot r + \\ b^2 \cdot x^2 \cdot r] \cdot y = 0 \end{aligned}$$

From the Eq. (5) obtained:

$$a = 1$$

$$r = 0$$

$$p = \frac{1}{s} \sqrt{\frac{(1-a)^2}{2}} - c = 0$$

$$b = 0 \quad s = 0 \quad p = 0$$

$$c = 0 \quad d = -4.k.C_o \quad \sqrt{\frac{d}{s}} = \text{imaginary}$$

Until the settlement of Eq. (16) are:

$$U = C_1 Z_p(\sqrt{4.k.C_o.z}) + C_2 Z_p(\sqrt{4.k.C_o.z}) \quad \dots(18)$$

At $t = 0, z = 0 \rightarrow z_p = \sim$

So $C_2 = 0$

$$U = C_1 Z_p(\sqrt{4.k.C_o.z})$$

Because $p = 0$ and $= \text{imaginary} \sqrt{d/s}$

$$\text{Then } U = C_1 I_0(\sqrt{4.k.C_o.z})$$

$$\frac{dU}{dt} = \frac{d}{dz} C_1 I_0(\sqrt{4.k.C_o.z}) \quad \dots(19)$$

From Sherwood page 178 pers. (5.83) got

$$\frac{dU}{dt} = C_1(\sqrt{4.k.C_o.z}) I_0(\sqrt{4.k.C_o.z}) \quad \dots(20)$$

From the original substitution, we get:

$$\frac{dU}{dt} = 2.k.C_z.C_1.I_0(\sqrt{4.k.C_o.z}) \quad \dots(21)$$

Then the press. (14) and (15) are obtained:

$$C_1.(\sqrt{4.k.C_o.z}) I_0(\sqrt{4.k.C_o.z}) = k.C.C_1.I_0(\sqrt{4.k.C_o.z})$$

$$C = \frac{(\sqrt{4.k.C_o.z}) I_0(\sqrt{4.k.C_o.z})}{k.C.C_2.I_0(\sqrt{4.k.C_o.z})}$$

$$C = \frac{C_o T_1(2\sqrt{k.C_o.T})}{k.t.T_o(2\sqrt{k.C_o.T})} \quad \dots(22)$$

b. Second Stage

At this stage the process runs continuously, but the steady state has not yet been reached. Can be expressed by:

$$C = f(t) \text{ and } V = \text{constant} \rightarrow dV/dt = 0$$

From the mass balance of the components obtained:

$$\frac{d}{dt}(V.C) = F.C_o - F.C - k.V.C^2 \quad \dots(23)$$

$$V.\frac{dC}{dt} - C.\frac{dV}{dt} = F.C_o - F.C - k.V.C^2 \quad \dots(24)$$

If $T = t - \check{T}$, time, minutes

$\check{T} = V/F$ time constant

Pers. (24) to be

$$\frac{dC}{dt} = \frac{C_0}{\check{T}} - \frac{C}{\check{T}} - k \cdot C^2 \quad \dots(25)$$

At steady state $C=C_0$

The settlement of the particular press. (25) is $C - C_s$, where C_s is the concentration at steady state.

Substitute $C = C_s + 1/s$

Pers. (25) turns into a first-order differential equation which can be solved by the integration factor method.

$$C = C_0 = \frac{1}{B \cdot \exp(AT) - \frac{K}{A}} \quad \dots(26)$$

C_1 is the initial concentration of each second stage at the time $t = \check{T}$ obtained by measuring the concentration of the sample.

c. Third phase

At this stage the process is running in a steady state and accumulation = 0 from the component balance, we get:

$$F - C_0 = F \cdot C + Vr \quad \dots(27)$$

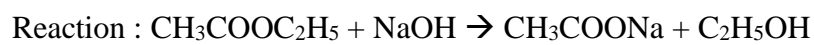
$$F - C_0 = F \cdot C + V \cdot k \cdot C_s^2 \quad \dots(28)$$

$$C_0 = C_s + (V/F) \cdot k \cdot C_s^2 \quad \dots(29)$$

$$k \cdot \check{T} \cdot C_s^2 + C_s - C_0 = 0 \quad \dots(30)$$

If k is known then C_s can be predicted. On the other hand, if C_s is measured, the value of k can be calculated. Eq. (30) is an ordinary algebraic equation and can be solved easily.

2.3 Thermodynamics Overview



To determine whether the reaction is exothermic/endothermic, it is necessary to prove it by using the standard heat of formation (ΔH_f) at 1 atm and 298 K of the reactants and products.

$$\Delta H_{298} = \Delta H \text{ reactants} - \Delta H \text{ products}$$

The data are known as follows (Smith et al., 2011)

$$\Delta H \text{ CH}_3\text{COOC}_2\text{H}_5 = -445,500 \text{ J/mol}$$

$$\Delta H \text{ NaOH} = -425,609 \text{ J/mol}$$

$$\Delta H \text{ CH}_3\text{COONa} = -726,100 \text{ J/mol}$$

$$\Delta H \text{ C}_2\text{H}_5\text{OH} = -235,100 \text{ J/mol}$$

So that :

$$\begin{aligned}\Delta H_{\text{reaction}} &= (\Delta H_{\text{CH}_3\text{COONa}} + \Delta H_{\text{C}_2\text{H}_5\text{OH}}) - (\Delta H_{\text{CH}_3\text{COOC}_2\text{H}_5} + \Delta H_{\text{NaOH}}) \\ &= ((-726,100 - 235,100) - (-445,500 - 425,609)) \text{ J/mol} \\ &= -91,091 \text{ J/mol}\end{aligned}$$

Because the ΔH of the reaction is negative, the reaction that takes place is an exothermic reaction that produces heat.



To determine the nature of the reaction whether it goes irreversible or reversible, it can be seen from the value of the reaction equilibrium constant.

At room temperature the data obtained (Smith et al., 2011):

$$\begin{aligned}\Delta G_{\text{CH}_3\text{COOC}_2\text{H}_5} &= -328,000 \text{ J/mol} \\ \Delta G_{\text{NaOH}} &= -379,494 \text{ J/mol} \\ \Delta G_{\text{CH}_3\text{COONa}} &= -631,200 \text{ J/mol} \\ \Delta G_{\text{C}_2\text{H}_5\text{OH}} &= -168,490 \text{ J/mol}\end{aligned}$$

So that :

$$\begin{aligned}\Delta G_{\text{reaction}} &= (\Delta G_{\text{CH}_3\text{COONa}} + \Delta G_{\text{C}_2\text{H}_5\text{OH}}) - (\Delta G_{\text{CH}_3\text{COOC}_2\text{H}_5} + \Delta G_{\text{NaOH}}) \\ &= (-631,200 - 168,490) - (-328,000 - 379,494) \text{ J/mol} \\ &= -92,196 \text{ J/mol}\end{aligned}$$

$$\frac{d}{dT} \left(\frac{\Delta G}{RT} \right) = \frac{\Delta H}{RT^2}$$

$$G = RT \ln K$$

$$K \text{ at standard } 298 \text{ K} = e^{(\Delta G/RT)}$$

$$K = e^{\frac{-92,196}{8.314 \cdot 298}} = 1.45 \times 10^{16}$$

From the above data, it can be obtained that the value of the reaction equilibrium constant at a temperature of 298 K is 1.45×10^{16} . At the operating temperature, the value of K is calculated by the equation:

$$\ln \left(\frac{K}{K'} \right) = \frac{-\Delta H^o}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right)$$

$$T = 27^\circ\text{C} \text{ (room temperature)} = 300 \text{ K}$$

$$\ln \left(\frac{1.45 \times 10^{16}}{K'} \right) = \frac{-(-91,091)}{8.314} \left(\frac{1}{300} - \frac{1}{298} \right)$$

$$K' = 1.13 \times 10^{16}$$

Because the value of the equilibrium constant is not close to “number” 1, the reaction proceeds in the same direction (irreversible).

2.4 Kinetics Overview

In terms of reaction kinetics, the speed of the saponification reaction of ethyl acetate with NaOH will increase with increasing temperature, stirring and concentration differences. This can be explained by the Arrhenius equation, namely:

$$k = k_0 \cdot e^{-\left(\frac{E_A}{RT}\right)}$$

With:

k = Reaction rate constant

k₀ = Pre-exponential factor or frequency

T = Temperature

E_A = Activation energy

R = Ideal gas constant

= 1.98 cal/gm-mol. K

= 1.98 Btu/lb-mol. °R

= 82.06 cm³.atm/gm-mol. K

Based on the Arrhenius equation, it can be seen that the reaction rate constant is influenced by the value of the frequency factor or exponential factor, temperature, and activation energy (Levenspiel, 1999).

2.5 Physical and Chemical Properties of Reagents

1. NaOH

Physical Properties:

- Molecular weight = 40 gr/mol
- Boiling point = 134⁰C
- Melting point = 318.4⁰C
- Specific gravity = 2.130 g/mol
- Solubility in 100 parts of cold water 10⁰C = 42
- Solubility in 100 parts of hot water 100⁰C = 32

Chemical Properties:

- With Pb(NO₃)₂ it forms a precipitate of Pb(OH)₂ which is soluble in excess reagent, is a strong base, and easily soluble in water.

2. Ethyl Acetate

Physical Properties:

- Specific gravity = 1,356 g/mol
- Boiling point = 85⁰C
- Molecular weight = 88 g/mol

- Melting point = -111°C

Chemical Properties:

Reacts with Hg^+ to form white Hg_2Cl_2 precipitate which is insoluble in hot water and dilute acid but soluble in dilute ammonia and KCN thiosulfate, reacts with Pb^{2+} to form white PbCl_2 , volatile when heated.

3. HCl

Physical Properties:

- Atomic mass = 36.45 gr/mol
- Density = 3.21 gr/ml
- Melting point = -101°C
- Ionization energy = 1250 kJ/mol
- Specific heat = $0.115\text{cal/gr}^{\circ}\text{C}$
- At room temperature HCl is a colorless gas with a pungent odor

Chemical Properties:

- HCl will smoke thickly in humid air
- The gas is greenish yellow in color and has a stimulating smell
- Soluble in alkali hydroxide, chloroform and ether
- Is a strong oxidizing agent
- Great affinity for other elements that can be toxic to the breath

2.6 Determining the Order of Reaction

Trial order of reaction in a batch reactor:

1. Given time data (t) and C_a , C_{a0} is C_a at $t=0$
2. Create data $-\ln(C_a/C_{a0})$ and $1/C_a$
3. First guess the 'first order reaction' by graphing $-\ln(C_a/C_{a0})$ vs t, the resulting graph should be straight.
 - a. If the result of the graph is not straight then guess the 'second order reaction' from the graph between $1/C_a$ vs t, the result of the graph must be straight (If $C_{a0}=C_{b0}$)
 - b. If the graph results are not straight then guessing the 'second order reaction' from the graph between $\ln C_b/C_a$ vs t, the graph results must be straight.
4. Form the equation $y = a + bx$, where a = intercept and b = slope of the $\log t$ vs $\ln C_{a0}$ graph.

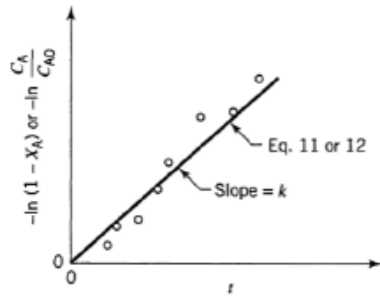


Figure 2.2 1st Order reaction trial graph

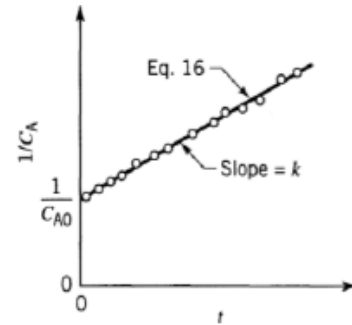


Figure 2.3 2nd Order reaction trial graph
($C_{A0} = C_{B0}$)

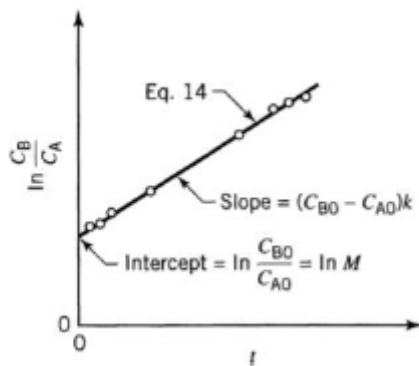


Figure 2.4 2nd Order reaction trial graph
($C_{A0} \neq C_{B0}$)

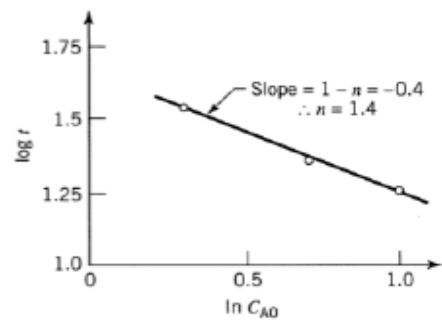
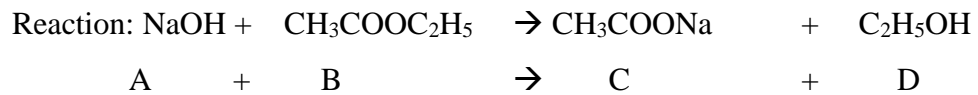


Figure 2.5 n Order reaction trial graph

2.7 Calculating the Saponification Reaction Constant (k) Ethyl Acetate with NaOH



Reaction order 1

$$-r_a = -\frac{dC_a}{dt} = k \cdot C_a$$

$$\int_{C_{a0}}^{C_a} -\frac{dC_a}{C_a} = \int_0^t k \cdot dt$$

$$-\ln[C_a]_{C_{a0}}^{C_a} = k \cdot t$$

$$-(\ln C_a - \ln C_{a0}) = k \cdot t$$

$$-\ln \frac{C_a}{C_{a0}} = k \cdot t$$

$$y = mx$$

Reaction order 2

The reaction rate equation:

$$-r_a = -\frac{dC_a}{dt} = k \cdot C_a \cdot C_b \text{ where } C_a = C_b$$

$$-\frac{dC_a}{dt} = k \cdot C_a^2$$

$$-\frac{dC_a}{C_a^2} = k \cdot dt$$

$$\int_{C_{ao}}^{C_a} -\frac{dC_a}{C_a^2} = \int_0^t k \cdot dt$$

$$\left[\frac{1}{C_a} \right]_{C_{ao}}^{C_a} = k \cdot t$$

$$\frac{1}{C_a} - \frac{1}{C_{ao}} = k \cdot t$$

$$\frac{1}{C_a} = k \cdot t + \frac{1}{C_{ao}}$$

$$y = mx + c$$

The value of k is obtained from the least square method. Where the value of k is the value of m.

(Levenspiel. O., 1970)

CHAPTER III PRACTICUM METHOD

3.1 Materials and Tools Used

3.2.1 Materials Used

1. NaOH
2. Ethyl Acetate
3. HCl
4. MO indicator 3 drops
5. Aquadest

3.2.2 Tools used

1. Pipette
2. Thermometer
3. Batch reactor
4. Measuring cup
5. Burette
6. Statives and Clamps
7. Erlenmeyer
8. Continuous flow reactor circuit

3.2 Experiment Circuit Drawing

a. Batch Process

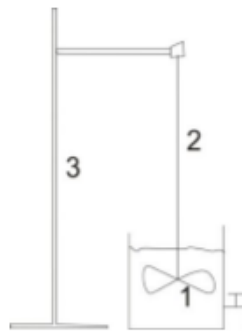


Figure 3.1 Batch process main tool drawing

Information :

1. Batch reactor
2. Stirrer
3. Stative

b. Continuous Process

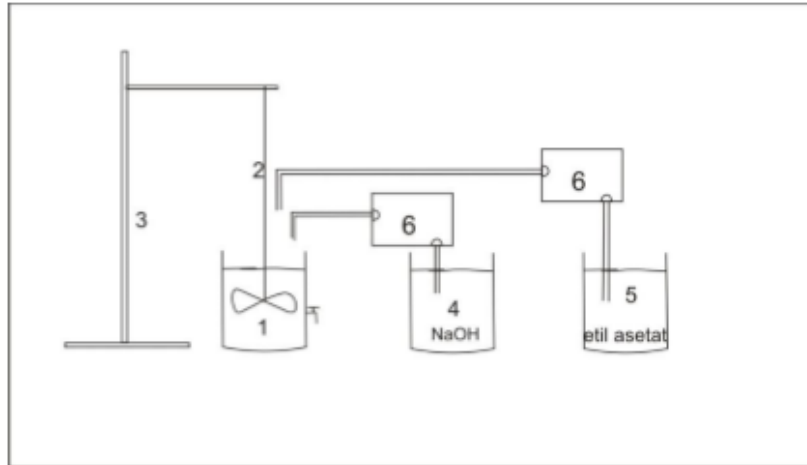


Figure 3.2 Continuous process main tool drawing

Information :

1. Continuous reactor
2. Stirrer
3. Stative
4. reactor tank

3.3 Response Test Results

The residual NaOH concentration that can be observed with the titrant concentration of HCl to ET (Endpoint Titration)

3.4 Trial Procedure

a. Batch Trial

1. Prepare the required reagent: ethyl acetate 0.1 N, HCl 0.05 N, and NaOH 0.1N.
2. Enter ethyl acetate 0.1 N and NaOH 0.1N with a volume of 1 liter each.
3. Take 5 ml sample every 1.5 minutes, then add 3 drops of MO indicator into the sample and titrate with HCl 0.1 N until it turns orange red. The titration was stopped until the volume of titrant used was constant 3 times.
4. By calculation, the value of Ca (residual NaOH concentration) can be obtained.
5. Perform steps 1 to 4 with different variables.

b. Continuous Trial

1. Prepare the required reagents: 0.1 N ethyl acetate, 0.1 N HCl, and 0.1 N NaOH.
2. Put ethyl acetate and NaOH into each feed tank.

3. Pump each reactant into the empty CSTR and keep the flow rate constant and react
4. Take 5 ml samples every 1 minute, then add 3 drops of MO indicator into the sample and titrate with HCl 0.1 N until it turns orange red. The titration was stopped until the volume of titrant used was constant 3 times.
5. By calculation, the value of Ca (residual NaOH concentration) can be obtained.
6. Perform steps 1 to 5 with medium and fast stirring.

HAZARD IDENTIFICATION AND RISKS ANALYST
MATERIAL: THE IDEAL CONTINUOUS FLOW REACTOR

HAZARD IDENTIFICATION (HI)											
A	Mechanic		D	Environment		E	Chemical Material		G	Other hazard	
A1	Manual handling	√	D1	Noise		E1	Toxicity	√	G1	Compressed gas	
A2	Moving part		D2	Vibration	√	E2	Irritant		G2	Ionic radiation	
A3	Rotating part	√	D3	Light		E3	Corosive	√	G3	UV radiation	
A4	Cutting		D4	Humidity		E4	Carcinogenic		G4	Fatigue	
B	Biology		D5	Temperature	√	E5	Flammable	√	G5	Narrow space	
B1	Bacterial		D6	Travel hazard		E6	Explosive		G6	Crowded	
B2	Virus		D7	Slippery surface		E7	Cryogenics		G7	Thermometer	√
B3	Fungi		D8	Solid waste		F	Equipments				
C	Electricity		D9	Air quality		F1	Pressure vessel				
C1	High Voltage		D10	Solitary work		F2	Hot equipments				
C2	Electrostatic		D11	Splash/water drop/flood	√	F3	Laser				
C3	Cable	√	D12	Powder spill		F4	Glass vessel				

RISKS							
HI	Risks (after action)				Risk Identification	Action to Minimize Risks	First Aid Action
	High	Medium	Low	Minimal			
1. PREPARATION							
			√		NaOH, HCl, and Ethyl Acetate preparation	<ul style="list-style-type: none"> - Make sure to always wear gloves when taking solutions, especially HCl solutions in the acid room - Always turn on the fan in the acid chamber, if you are taking HCl solution - Always wear complete lab equipment, such as lab coats, gloves, shoes, and medical masks 	<ul style="list-style-type: none"> - Wash hands if exposed to related solutions - If it accidental hurts, immediately ask for further help
2. MAIN EXPERIMENTS							
			√		When starting the pump there is a risk of electric shock, or the pump will catch fire	<ul style="list-style-type: none"> - Make sure the cable / plug is not wet - Always wear complete lab equipment, such as lab coats, gloves, shoes, and medical masks 	<ul style="list-style-type: none"> - Turn off the power source - Push the victim's body with an insulating object - Immediately ask for first aid
3. ANALYSYS/FINAL STAGE							
					NaOH, HCl, and Ethyl Acetate waste disposal	<ul style="list-style-type: none"> - Make sure each of chemicals have their own place to be disposed - Always wear complete lab equipment, such as lab coats, gloves, shoes, and medical masks 	<ul style="list-style-type: none"> - Wash hands if exposed to related solutions - If it accidental hurts, immediately ask for further help

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