

CHAPTER I

INTRODUCTION

1.1 Background

Chemical reactions applied in the chemical industry can involve raw materials of different forms, either in the form of solids, gases, or liquids. Therefore, chemical reactions in an industry can occur in multiple or heterogeneous phases, for example, binary or even tertiary (Coulson, 1996). Before the chemical reaction takes place, one or more raw materials (reactants) will move from the mainstream to the interphase/boundary layer or to the mainstream of other raw materials that are in a different phase.

Gas-liquid absorption is a heterogeneous process involving the transfer of a soluble gas component to an absorber, usually a non-volatile liquid (Franks, 1967). Chemical reactions in the absorption process can occur in the gas layer, the interphase layer, the liquid layer, or even the main body of the liquid, depending on the concentration and reactivity of the reacting materials. To facilitate these process stages, the absorption process is usually carried out in a stirred tank reactor with a sparger, a bubble column, or a packed bed column. The gas-liquid absorption process can be applied to the purification of synthesis gas which is still helpful in flue gas or even in industries involving gas dissolution in a liquid, such as H_2SO_4 , HCl , HNO_3 , formaldehyde, and others (Coulson, 1996). The absorption of CO_2 gas with a strong hydroxide solution is an absorption process accompanied by a second-order chemical reaction between CO_2 and OH^- ions to form CO_3^{2-} and H_2O ions. Meanwhile, the reaction between CO_2 and CO_3^{2-} to form HCO_3^- ions are usually neglected (Danckwerts 1970; Juvekar & Sharma, 1972). However, according to Rehm et al. (1963), this process is also usually considered to follow a first-order reaction if the concentration of the NaOH solution is relatively low (dilute).

Chemical reactor design is based on the hydrodynamic modeling of the reactor and the chemical reactions that occur in it. A mathematical model is a simplified form of the actual process in a reactor which is usually very complex (Levenspiel, 1972). Chemical reactions are usually studied in a laboratory-scale batch process by considering the needs of the reactants, ease of reaction control, equipment, ease of carrying out reactions and analysis, and accuracy.

1.2 Formulation of the problem

1. How influence operating variable on the amount of CO₂ absorbed at various reaction times?
2. How influence operating variable on the value of the mass transfer coefficient of gas-phase CO₂ (k_{Ga})?
3. How influence operating variable on the value of the mass transfer coefficient of liquid phase CO₂ (k_{La})?
4. How influence operating variable on the value of the reaction constant between CO₂ and NaOH (k_2)?

1.3 Practicum Purpose

After conducting this experiment, students can explain the following things:

1. Effect of operating variables on the amount of CO₂ absorbed at various reaction times.
2. Effect of operating variable on the value of the mass transfer coefficient of gas-phase CO₂ (k_{Ga}).
3. Effect of operating variable on the value of the mass transfer coefficient of liquid phase CO₂ (k_{La}).
4. Effect of operating variable on the value of the reaction constant between CO₂ and NaOH (k_2).

1.4 Practicum Benefits

Students can understand the reactions that occur in reactants in the form of gas and liquid (heterogeneous) and apply them in research on reactor design and related process tools.

CHAPTER II LITERATURE REVIEW

2.1 Absorption

Absorption is one of the separation processes in the chemical industry where a gas mixture is contacted with an absorbing liquid so that one or more of the gas components dissolve in the liquid. Absorption can occur through two mechanisms, namely physical absorption, and chemical absorption.

Physical absorption is a process that involves the dissolution of gas in an absorbent solution but is not accompanied by a chemical reaction. An example of this process is the absorption of H_2S gas with water, methanol, and propylene carbonate. Absorption occurs due to physical interactions. The mechanism of the physical absorption process can be explained by several models, namely: two films theory by Whitman (1923), the penetration theory by Dankwerts, and the surface renewal theory.

Chemical absorption is a process that involves the dissolution of gas in an absorbent solution accompanied by a chemical reaction. An example of this event is the absorption of CO_2 gas with a solution of MEA, NaOH, K_2CO_3 , and etc. The application of chemical absorption can be found in Ammonia plants CO_2 gas absorption process, as shown in figure 2.1.

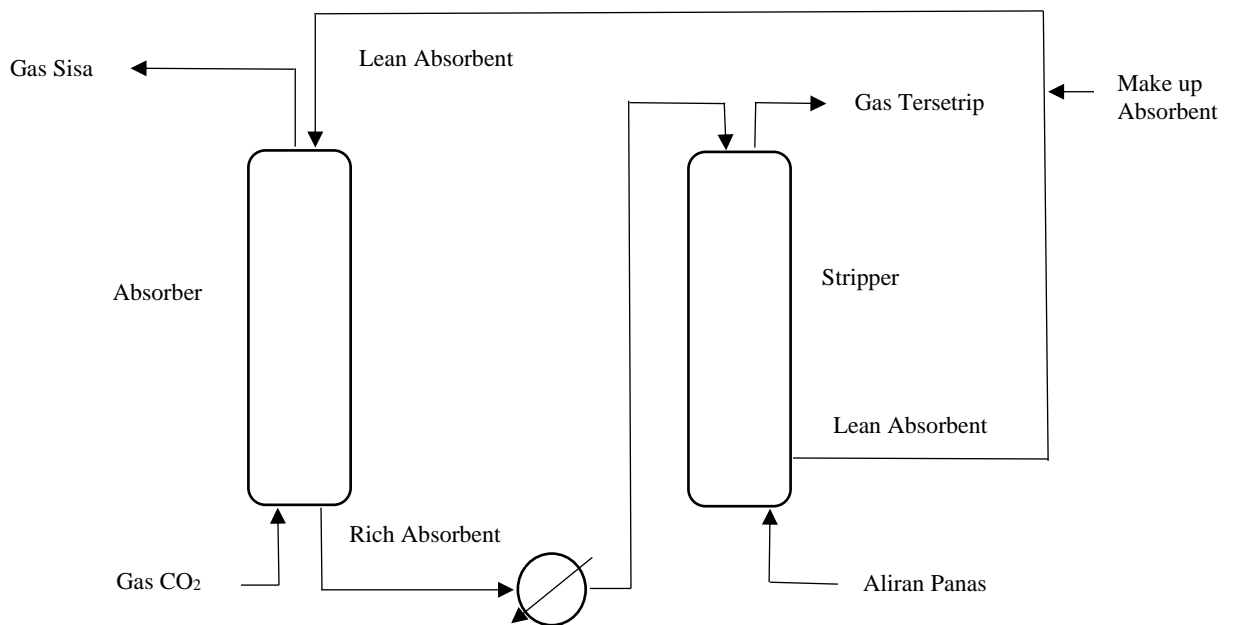


Figure 2.1 CO_2 absorption and desorption process with MEA solvent in
Ammonia factory

The absorption process can be carried out in a stirred tank equipped with a sparger, a bubble column, a packed column, or a tray column. The selection of

absorption process equipment is usually based on the reactivity of the reactants (gas and liquids), temperature, pressure, capacity, and economy.

2.2 Absorption Column

Absorption column is a column or tube where the process of absorption (absorption) of the substance that is passed in the column/tube occurs. In general, there are four types of absorption columns: spray towers, bubble columns, tray columns and packed bed columns.

2.2.1 Spray tower (spray column)

In a spray tower the gas phase flows up through a large open space and the liquid phase is introduced using a nozzle or other means of spraying. The liquid that is fed in the form of fine drops falls with a current that is in the opposite direction to the rising gas current.

2.2.2 Bubble column

The bubble tower consists of large open spaces through which the liquid phase flows into these spaces and gas will be dispersed into the liquid phase in the form of fine bubbles. Small gas bubbles will provide the desired contact area, rising bubbles create a mixing action in the liquid phase, thereby reducing the liquid phase's resistance to mass transfer. Bubble towers are used with systems where the liquid phase usually controls the mass transfer rate.

2.2.3 Tower Plate (tray column)

Plate towers or tray columns are towers that are widely used in industry. This tower consists of several types, namely: Sieve Tray, Valve Tray and Bubble Cup Tray.

2.2.4 Tower Packing (packed bed column)

Packing tower is a tower filled with filler material. The function of the filler is to expand the contact area between the two phases. Inside the tower, the liquid will flow downward through the lower surface of the fill, while the gas will flow upward in a countercurrent, through the void space between the fill.

2.3 Analysis of Mass Transfer and Reaction in the Process Absorption of Gases by Liquids

In general, the process of absorption of CO₂ gas into a NaOH solution accompanied by a chemical reaction takes place through four stages, namely the mass transfer of CO₂ through the gas layer to the gas-liquid interphase layer, equilibrium between CO₂ in the gas phase and in the solution phase, mass transfer of CO₂ from the gaseous layer to the main body of the NaOH solution and the reaction between dissolved CO₂ and the hydroxyl group (OH⁻). The schematic of the process can be seen in Figure 2.2.

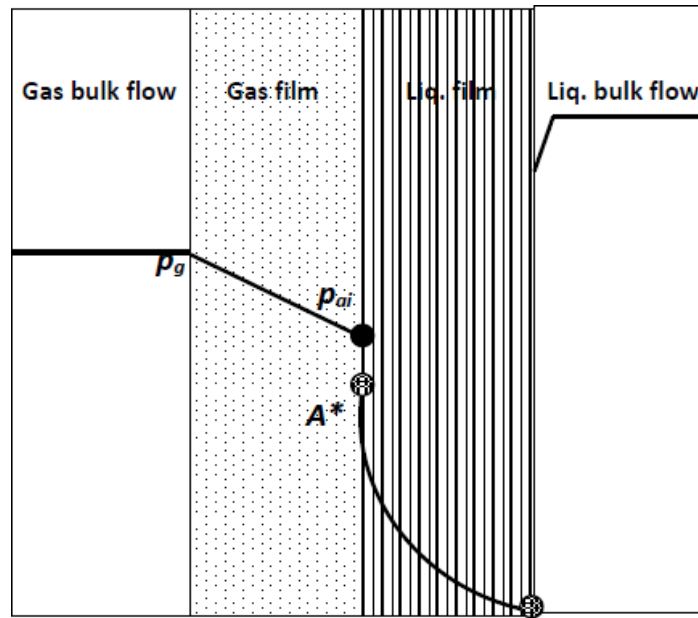


Figure 2.2 The absorption mechanism of CO₂ gas in NaOH solution

Mass transfer rate of CO₂ through the gas layer:

$$R_a = k_g a (p_g - p_{ai}) \quad (2.1)$$

Equilibrium between CO₂ in the gas phase and in the solution phase:

$$A^* = H \cdot p_{ai} \quad (2.2)$$

with H at 30 °C = 2,88.10⁻⁵ g mol/cm³. atm.

The rate of mass transfer of CO₂ from the gas layer to the main body of the NaOH solution and the reaction between dissolved CO₂ and the hydroxyl group:

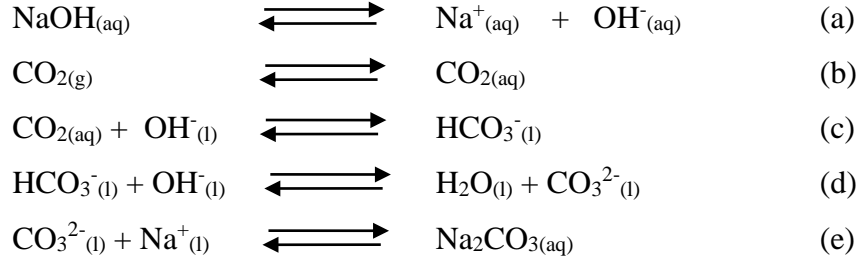
$$R_a = [A^*] a \sqrt{D_A k_2 [\text{OH}^-]} \quad (2.3)$$

Boundary state :

$$(a) \frac{\sqrt{D_A k_2 [\text{OH}^-]}}{k_L} \gg \gg 1$$

$$(b) \frac{\sqrt{D_A k_2 [\text{OH}^-]}}{k_L} \ll \ll \frac{[\text{OH}^-]}{z \cdot A^*} \sqrt{\frac{D_A}{D_B}}$$

where z is the coefficient of the chemical reaction between CO₂ and [OH⁻], which is = 2. In the liquid phase, the reaction between CO₂ and NaOH solution occurs through several process steps:



Steps d and e generally take place very quickly, so the dissolution of CO₂ usually controls the absorption process into NaOH solution, especially if CO₂ is fed in the form of a mixture with other gases or held together with the chemical reaction in step c (Juvekar & Sharma, 1973).

Elimination A* from equations 1, 2, and 3 gives:

$$R_a = \frac{a.H.p.g.\sqrt{D_{A.k_2.[OH^-]}}}{a.H.\sqrt{D_{A.k_2.[OH^-]}} + \frac{k_{Ga}}{1}} \quad (2.4)$$

If the value of k_L is very large, then : $\frac{\sqrt{D_{A.k_2.[OH^-]}}}{k_L} \approx 1$ so that the above equation becomes :

$$R_a = \frac{a.H.p.g.\sqrt{D_{A.k_2.[OH^-]+k_L^2}}}{a.H.\sqrt{D_{A.k_2.[OH^-]+k_L^2}} + \frac{k_{Ga}}{1}} \quad (2.5)$$

If the boundary condition (b) is not met, it means that [OH⁻] is stripped from the solution. This results in:

$$\frac{\sqrt{D_{A.k_2.[OH^-]}}}{k_L} \approx \frac{[OH^-]}{z.A^*} \sqrt{\frac{D_A}{D_B}} \quad (2.6)$$

Thus, the absorption rate of CO₂ gas into NaOH solution will follow the equation:

$$R_a = \frac{a.H.p.g.\phi k_L}{1 + \frac{a.H.\phi k_L}{k_{Ga}}} \quad (2.7)$$

Where ϕ is the enhancement factor which is the ratio between the mass transfer coefficient of CO₂ in the liquid phase if the absorption is accompanied by a chemical reaction and not accompanied by a chemical reaction as formulated by Juvekar and Sharma (1973):

$$\phi = \frac{\sqrt{D_{A.k_2.[OH^-]}}}{k_L} \cdot \left[\frac{1 + \frac{[OH^-]D_B}{z.A^*D_A}\phi}{\frac{[OH^-]D_B}{z.A^*D_A}} \right]^{1/2} \quad (2.8)$$

The effective diffusivity (D_A) of CO₂ in NaOH solution at 30 °C is 2,1 x 10⁻⁵ cm²/det (Juvekar & Sharma, 1973).

The value of k_{Ga} can be calculated based on physical absorption by observing the total mass transfer of CO₂ into NaOH solution that occurs at a certain time in the absorption apparatus. In the form of a dimensionless number, k_{Ga} can be

calculated according to the equation (Kumoro & Hadiyanto, 2000):

$$\frac{k_{Ga} dp^2}{D_A} = 4,0777 \times \left(\frac{\rho_{CO_2} \cdot Q_{CO_2}}{\mu_{CO_2} \cdot a} \right)^{1,4003} \times \left(\frac{\mu_{CO_2}}{\rho_{CO_2} D_A} \right)^{1/3} \quad (2.9)$$

With $a = \frac{6(1-\epsilon)}{dp}$ and $\epsilon = \frac{V_{void}}{V_T}$

Theoretically, the value of k_{Ga} must satisfy the equation:

$$k_{Ga} = \frac{\text{mol}(CO_2, \text{liq})}{A \cdot Z \cdot \epsilon \cdot p_{im}} = \frac{\text{mol}(CO_3^{2-})}{A \cdot Z \cdot \epsilon \cdot p_{im}} \quad (2.10)$$

If the operating pressure is low enough, then p_{im} can be approached with $\Delta p = p_{in} - p_{out}$

While the value k_{La} can be calculated empirically with the equation (Zheng & Xu, 1992):

$$\frac{k_{La} \cdot dp}{D_A} = 0,2258 \times \left(\frac{\rho_{NaOH} \cdot Q_{NaOH}}{\mu \cdot a} \right) \times \left(\frac{\mu}{\rho \cdot D_A} \right)^{0,5} \quad (2.11)$$

Suppose the reaction rate for the formation of Na_2CO_3 is much greater than the rate of diffusion of CO_2 into the $NaOH$ solution. In that case, the concentration of CO_2 at the boundary between the liquid film and the liquid body is zero. This is due to the very fast consumption of CO_2 during the reaction throughout the film.

Thus the thickness of the film (x) can be determined by the equation:

$$x = \frac{D_A \cdot (\rho_{in} - \rho_{out})}{\text{mol}(CO_3^{2-}) \cdot R \cdot T} \quad (2.12)$$

CHAPTER III PRACTICUM METHOD

3.1 Materials and Tools Used

1. Materials used

1. Crystalline sodium hydroxide (NaOH)
2. Carbon dioxide gas (CO₂) is stored in a pressurized tube
3. Air
4. Aquadest (H₂O)
5. Reagents for analysis are HCl solution, PP indicator, and MO

2. Tools used

The series of absorption practicum tools is shown in Figure 3.1

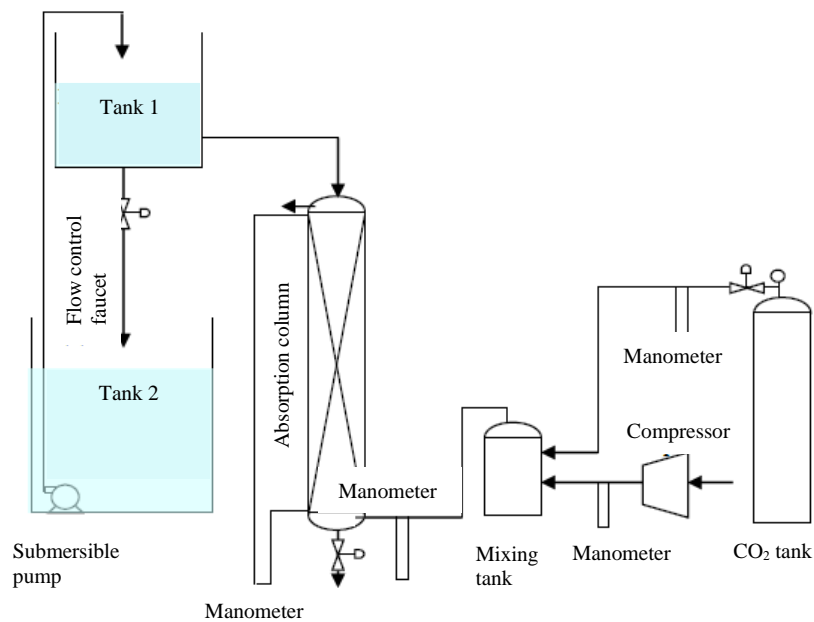


Figure 3.1 Main set of tools

3.2 Response Test Results

The concentration of CO₃²⁻ ions in the sample solution and CO₂ absorbed.

3.3 Practical Procedure

1. Making NaOH mother liquor

The NaOH solution is made by weighing ... gram of NaOH and dissolved in 10 L of aquadest, and then the NaOH solution is accommodated in a tank for use.

2. Determine the fraction of free space in the absorption column

First, the faucet under the absorption column is in the closed position. After that, drain the NaOH solution from reservoir 2 into the absorption column.

Next, stop the flow of the liquid level in the column is exactly as high as the packing pile. Remove the flow in the column by opening the valve at the bottom of the column, and the liquid is accommodated in an Erlenmeyer or measuring cup. Then the valve is closed if the liquid in the column is right at the bottom of the packing. Record the volume of liquid as the volume of free space in the absorption column = V_{void} . Determine the total volume of the absorption column, by measuring the column diameter (D) and $V_T = \frac{\pi D^2 \cdot H}{4}$ the packing stack height (H). Then calculate the empty space fraction of absorption column $\varepsilon = \frac{V_{\text{void}}}{V_T}$.

3. Absorption operation

The absorption operation is carried out by pumping a variable NaOH solution into the column through the top of the column at a specific flow rate until a steady-state is reached. Next, pass CO₂ gas through the bottom of the column and measure the difference in liquid level in the manometer. Then take 10 mL of the liquid sample from the bottom of the absorption column every 1 minute for 10 minutes and analyze the carbonate ion content or free NaOH content.

4. Analyze samples

First, take 10 mL of a liquid sample which is placed in an Erlenmeyer. Next, add three drops of PP indicator, and the sample is titrated with HCl solution according to the variable until the red color is almost gone (titrant requirement = a mL). Then add 2-3 drops of methyl orange (MO) indicator, and the titration is continued again until the orange color changes to red (titrant requirement = b mL).

3.4 Observation Sheet

3.4.1 Operating Variables

a. Fixed variable

1. CO₂ pressure: 6,5 bar
2. Temperature : 30°C
3. HCl concentration :

b. Variable changed

- NaOH concentration :
- NaOH flow rate :

3.4.2 Data

- Vvoid :
- $\Delta Z1$:
- $\Delta Z2$:
- $\Delta Z3$:

Variable 1

T (minutes)	Va (mL)	Vb (mL)
0		
1		
....		
10		

Variable 2

T (minutes)	Va (mL)	Vb (mL)
0		
1		
....		
10		

Variable 3

T (minutes)	Va (mL)	Vb (mL)
0		
1		
....		
10		

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HAZARD IDENTIFICATION AND RISK ANALYSIS
MATERIAL: CO2 ABSORPTION WITH NaOH SOLUTION

HAZARD IDENTIFICATION (IB)											
A	Mechanic		D	Environment		E	Material chemistry		G	Danger other	
A1	Manual handling	√	D1	Noise	√	E1	Poison		G1	Compressed gas	√
A2	Moving parts		D2	Vibration		E2	Irritant	√	G2	Radiation ionizing	
A3	Rotating part		D3	Lighting		E3	Corrosive	√	G3	UV radiation	
A4	Cutting		D4	Humidity		E4	carcinogenic		G4	Fatigue	
B	Biology		D5	temperature		E5	Easy burnt	√	G5	Narrow space	
B1	Bacteria		D6	Danger journey		E6	Easy explode		G6	Full congested	
B2	Virus		D7	Smooth surface _		E7	Cryogenics	√	G7	Thermometer	
B3	Mold		D8	Waste congested		F	Equipment				
C	Electricity		D9	Quality air	√	F1	Vessel press				
C1	Voltage tall	√	D10	Work solitary		F2	Equipment hot				
C2	Static electricity		D11	Splash / drip / flood		F3	Laser				
C3	Cable	√	D12	Spill powder		F4	vessels glass				

RISK DETAILS							
IB	Risk (after action control)				Identification risk	Control measures For minimize risk	Help action First
	Tall	Curre ntly	Low	At a minim um			
1. PREPARATION/EARLY STAGE							
		√			Risk irritation If caught NaOH solution	- Use PPE	- If swallowed, rinse mouth. Don't induce vomiting - In case of contact with skin (or hair), remove immediately all contaminated clothing and rinse skin with water or shower - In case of contact with eyes, rinse carefully with water for several minutes
2. MAIN EXPERIMENT							
		√			Moment turn on pump There is risk stung electricity / short circuit	- Make sure cables / plugs No wet , make sure / check fan on pump can rotate with Good so that pump No burnt - Use PPE & shoes rubber	- Turn off source current electricity - Push victim's body with insulating object - Get help medical - treat wound burn
		√					

RISK DETAILS							
IB	Risk (after action control)				Identification risk	Control measures For minimize risk	Help action First
	Tall	Curre ntly	Low	At a minim um			
			√		<p>Moment turn on compressor There is risk stung electricity / short circuit</p> <p>Noise consequence compressor</p> <p>Risk to health if CO₂ gas is flowing too big</p> <p>The mercury in the manometer is there risk go out from hose if CO₂ gas is</p>	<ul style="list-style-type: none"> - Make sure cables / plugs No wet - Use PPE & shoes rubber - Use ear plug PPE - Make sure flowing CO₂ gas in accordance with pressure already _ set practicum - Use PPE - Make sure flowing CO₂ gas in accordance with pressure 	<ul style="list-style-type: none"> - Turn off source current electricity - Push victim's body with insulating object - Get help medical - treat wound burn - Turn off source noise - rest ear - Get some fresh air and turn off the CO₂ gas flow - Perform CPR if necessary - If mercury contact with skin , exposed eye , or swallowed

RISK DETAILS							
IB	Risk (after action control)				Identification risk	Control measures For minimize risk	Help action First
	Tall	Curre ntly	Low	At a minim um			
					flowing too big	already _ set practicum - Use PPE	quick rinse with excess water
3. ANALYSIS/FINAL STAGE							
		√			Risk irritation If caught HCl solution when do titration	- Use PPE	<ul style="list-style-type: none"> - If swallowed, rinse mouth. Don't induce vomiting - In case of contact with skin (or hair), remove immediately all contaminated clothing and rinse skin with water or shower - In case of contact with eyes, rinse carefully with water for several minutes