CHAPTER 1
INTRODUCTION

1.1 Background

Chemical reactions applied in the chemical industry may involve raw materials of different physical states, such as solids, gases, and liquids. Therefore, chemical reactions in industry may occur in a single phase (homogeneous) or in multiple phases (heterogeneous), for example binary or even ternary systems (Coulson, 1996). Prior to the occurrence of a chemical reaction, one or more raw materials (reactants) will be transferred from their main flow to the interfacial layer or boundary, or toward the main flow of another reactant that exists in a different phase.

Gas–liquid absorption is a heterogeneous process involving the transfer of a soluble gas component into an absorbent, which is typically a non-volatile liquid (Franks, 1967). Chemical reactions in absorption processes may take place in the gas film, at the gas–liquid interface, in the liquid film, or even in the bulk liquid, depending on the concentration and reactivity of the reacting species. To facilitate these process stages, absorption is commonly carried out in stirred tank reactors equipped with spargers, bubble columns, or packed columns containing inert particles. Gas–liquid absorption processes are applied in the purification of synthesis gas that is still present in exhaust gases, as well as in industries involving gas dissolution in liquids, such as the production of H_2SO_4, HCl, HNO_3, formaldehyde, and others (Coulson, 1996). The absorption of CO_2 gas using strong hydroxide solutions is an absorption process accompanied by a second-order chemical reaction between CO_2 and OH^- ions, forming CO_3^{2-} ions and H_2O. Meanwhile, the reaction between CO_2 and CO_3^{2-} to form HCO_3^- ions is generally neglected (Danckwerts, 1970; Juvekar & Sharma, 1972). However, according to Rehm et al. (1963), this process is also commonly considered to follow first-order reaction kinetics when the concentration of the NaOH solution is sufficiently low (dilute).

The design of chemical reactors is based on the modelling of reactor hydrodynamics and the chemical reactions occurring within them. A mathematical model represents a simplification of the actual processes inside a reactor, which are typically highly complex (Levenspiel, 1972). Chemical reactions are usually studied through laboratory-scale batch processes, considering reactant requirements, ease of reaction control, equipment considerations, operational feasibility, analytical convenience, and accuracy.

1.2 Problem Formulation

1. How do operating variables affect the amount of CO_2 absorbed at various reaction times?
2. How do operating variables affect the value of the gas-phase CO_2 mass tranfer coefficient (k_{GA})?
3. How do operating variables affect the value of the liquid-phase CO_2 mass transfer coefficient (k_{LA})?
4. How do operating variables affect the value of the overall mass transfer coefficient between CO_2 and H_2O (K_{OG})?

1.3 Objectives of the Experiment

After conducting this experiment, students are expected to be able to perform and/or explain the following:

1. Prepare and operate the absorption system, analyze samples, and process experimental data.
2. The effect of variables on the amount of CO_2 absorbed at various reaction times.
3. The effect of variables on the value of the gas-phase CO_2 mass transfer coefficient (k_{GA}).
4. The effect of variables on the value of the liquid-phase CO_2 mass transfer coefficient (k_{LA}).
5. The effect of variables on the value of the overall mass transfer coefficient between CO_2 and H_2O (K_{OG}).

1.4 Benefits of the Experiment

(Students are required to independently identify and obtain information regarding the benefits of the experiment).

CHAPTER II
LITERATURE REVIEW

2.1 Absorption

Absorption is one of the separation processes in the chemical industry in which a gas mixture is brought into contact with a liquid absorbent, allowing one or more components of the gas to dissolve in the liquid. Absorption can occur through two mechanisms, namely physical absorption and chemical absorption.

2.1.1 Physical Absorption

Physical absorption is a process that involves the dissolution of a gas into an absorbing solution without being accompanied by a chemical reaction. Examples of this process include the absorption of H_2S gas by water, methanol, and propylene carbonate. Absorption occurs due to physical interactions between the gas and the liquid. The mechanism of physical absorption can be explained by several models, namely the two-film theory proposed by Whitman (1923), the penetration theory proposed by Danckwerts, and the surface renewal theory.

2.1.2 Chemical Absorption

Chemical absorption is a process that involves the dissolution of a gas into an absorbing solution accompanied by a chemical reaction. Examples of this process include the absorption of CO_2 gas using MEA (Mono Ethanol Amine), NaOH, K_2CO_3 (Potassium Carbonate), and others. Applications of chemical absorption can be found in the CO_2 gas absorption process in ammonia plants, as illustrated in Figure 2.1.

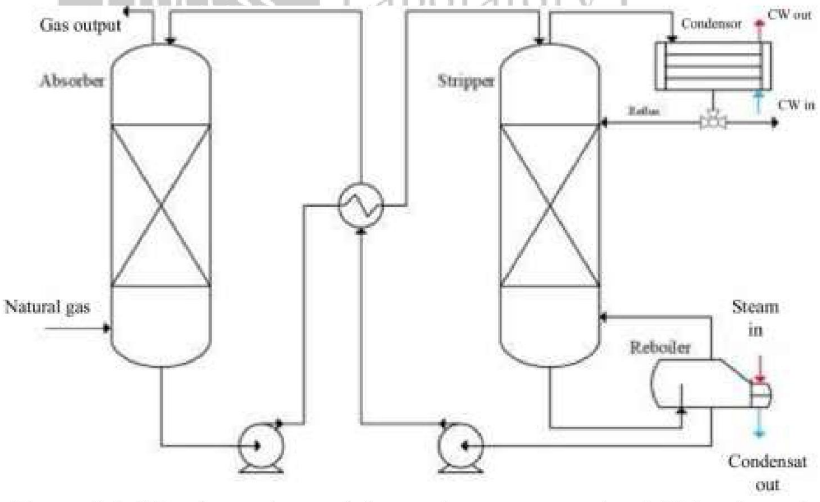

Figure 2.1 CO_2 absorption and desorption process using MEA solvent in an ammonia plant

The absorption process can be carried out in a stirred tank equipped with a sparger, a bubble column, a column packed with inert packing (packed column), or a tray column. The selection of absorption equipment is generally based on the reactivity of the reactants (gas and liquid), the corrosiveness of the absorbed component and the absorbent, operating temperature, pressure, capacity, and economic considerations.

2.2 Absorption Column

An absorption column is a column or vessel in which the absorption process of a substance passing through the column or vessel takes place. In general, there are four types of absorption columns, namely spray columns, bubble columns, tray columns, and packed bed columns.

2.2.1 Spray column

In a spray column (Figure 2.2), the gas phase flows upward through a large open space, while the liquid phase is introduced using nozzles or other spraying devices. The liquid is fed in the form of fine droplets and falls counter currently to the upward flow of the gas.

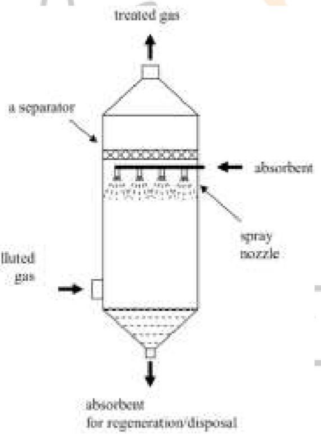

Figure 2.2 Spray column

2.2.2 Bubble column

A bubble column (Figure 2.3) consists of large open spaces through which the liquid phase flows, and the gas is dispersed into the liquid phase through a sparger located at the bottom of the column in the form of fine bubbles. The small gas bubbles provide the desired interfacial contact area, and the rising bubbles induce mixing action within the liquid phase, thereby reducing the resistance of the liquid phase to mass transfer. Bubble columns are used in systems where the liquid phase typically controls the rate of mass transfer.

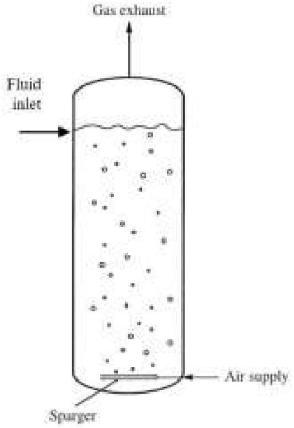

Figure 2.3 Bubble column

2.2.3 Plate column (tray column)

A plate column or tray column (Figure 2.4) is a type of column that has been widely used in industry. This column consists of several types, namely sieve trays, valve trays, and bubble cap trays. In a plate column, the liquid flows across each tray, passes over the outlet weir, and enters the downcomer, which carries the liquid by gravity to the tray below. The gas flows upward through the holes on each tray and forms bubbles as it passes through the liquid on the tray, thereby generating a frothy foam (Seader et al., 1997).

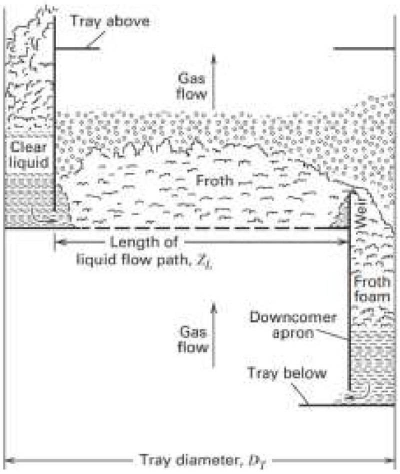

Figure 2.4 Plate column

2.2.4 Packed bed column

A packed column (Figure 2.5) is a column filled with packing materials. The function of the packing is to increase the interfacial contact area between the two phases. In this column, the liquid flows downward over the surface of the packing, while the gas flows upward counter currently through the void spaces between the packing materials. In packed columns, there are two types of packing materials, namely random packing and structured packing.

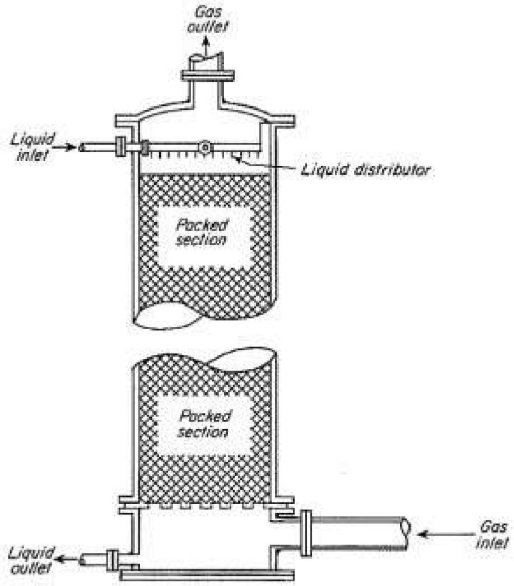

Figure 2.5 Packed column

In random packing, the packing materials occupy random positions within the column. Random packings are available in various materials, including ceramics, metals, plastics, and carbon. The selection of material for random packing is based on the properties of the liquid and the operating temperature. Ceramic materials are generally used for corrosive liquids, however, they are not suitable for use with strong alkalis. Plastic materials are generally susceptible to certain organic solvents and can only be used at moderate temperatures (Towler & Sinnott, 2008). Meanwhile, metal materials are more recommended for use under operating conditions that tend to be unstable, such as drastic changes in pressure, flow rate, and temperature, because ceramic and plastic materials tend to suffer damage under such conditions (Ludwig, 1997; Towler & Sinnott, 2008).

In contrast, in structured packing, the position of the packing materials is fixed and neatly arranged within the column. Packing materials in structured packings are made of wire mesh or perforated metal sheets. These materials are folded and arranged in a regular geometry to provide a high surface area. Materials used in structured packings are available in metal, plastic, and ceramic. The cost of structured packing is generally much higher than that of random packing, however, it offers higher efficiency (Towler & Sinnott, 2008).

Packed columns operated at high gas velocities may experience back-mixing, and excessively high gas velocities may cause flooding in the column. Conversely, low gas velocities can lead to a reduction in the mass transfer rate because the packing materials will not be uniformly wetted by the liquid (Silia, 2003).

2.3 Analysis of Mass Transfer and Reactions in Gas Absorption Processes by Liquids

In general, the absorption process of CO_2 gas into a NaOH solution accompanied by a chemical reaction proceeds through four stages, namely the mass transfer of CO_2 through the gas film toward the gas–liquid interfacial layer, the equilibrium between CO_2 in the gas phase and in the liquid phase, the mass transfer of CO_2 from the interfacial layer into the bulk NaOH solution, and the reaction between dissolved CO_2 and hydroxyl (OH^-) groups. The schematic of this process is shown in Figure 2.6.

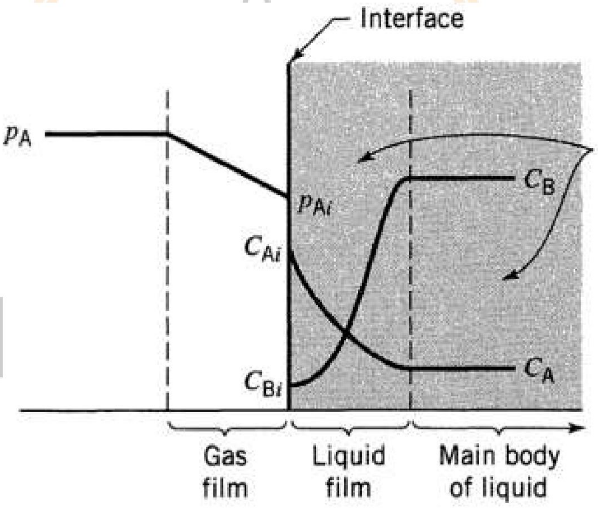

Figure 2.6 Mechanism of CO_2 gas absorption in NaOH solution

The rate of CO_2 mass transfer through the gas film:

$$R_a = k_{GA} (p_A - p_{Ai}) \tag{2.1}$$

The equilibrium between CO_2 in the gas phase and in the liquid phase:

$$p_{Ai} = H \times C_{Ai} \tag{2.2}$$

p_{Ai} = Partial pressure of gas A at the gas–liquid interface (atm)

p_A = Partial pressure of gas A in the gas phase (atm)

k_{GA} = Gas-phase mass transfer coefficient (mol/atm·min)

H = Equilibrium constant of gas A (atm·L/mol)

C_{Ai} = Concentration of A in the liquid phase at the gas–liquid interface with H at a temperature of 30°C = 2,88 $\times 10^{-5}$ g.mol/cm^3. atm.

The rate of CO_2 mass transfer from the gas film into the bulk NaOH solution and the reaction between dissolved CO_2 and hydroxyl groups:

$$R_a = [A^*]\ a \sqrt{D_A k_A\ [OH-]} \tag{2.3}$$

Boundary condition:

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

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

where z is the chemical reaction coefficient between CO_2 and $[OH^-]$, which is equal to 2. In the liquid phase, the reaction between CO_2 and the NaOH solution occurs through several process stages:

$$NaOH_{(aq)} \rightleftarrows Na^+_{(aq)} + OH^-_{(aq)} \tag{2.4}$$

$$CO_{2(g)} \rightleftarrows CO_{2(aq)} \tag{2.5}$$

$$CO_{2(aq)} + OH^-_{(l)} \rightleftarrows HCO_3^-{}_{(l)} \tag{2.6}$$

$$HCO_3^-{}_{(l)} + OH^-_{(l)} \rightleftarrows H_2O_{(l)} + CO_3^{2-}{}_{(l)} \tag{2.7}$$

$$CO_3^{2-}{}_{(l)} + 2Na^+_{(l)} \rightleftarrows Na_2CO_{3(aq)} \tag{2.8}$$

Steps d and e usually proceed very rapidly because they are ionic reactions; therefore, the absorption process is generally controlled by the dissolution of CO_2 into the NaOH solution, particularly when CO_2 is fed as a mixture with other gases, or is jointly controlled by the chemical reaction occurring in step c (Juvekar & Sharma, 1973).

Elimination of A* from Equations 2.1, 2.2, and 2.3 yields:

$$R_a = \frac{a.H.pA.\sqrt{D_A.k_2.[OH^-]}}{1+\frac{a.H.\sqrt{D_A.k_2.[OH^-]}}{k_{GA}}} \tag{2.9}$$

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

$$R_a = \frac{a.H.pA.\sqrt{D_A.k_2.[OH^-]+k_L{}^2}}{1+\frac{a.H.\sqrt{D_A.k_2.[OH^-]+k_L{}^2}}{k_{GA}}} \tag{2.10}$$

If boundary condition (b) is not satisfied, this indicates the occurrence of depletion of $[OH^-]$ in the solution. This results in:

$$\frac{\sqrt{D_A.k_2.[OH^-]}}{k_L} \approx \frac{[OH^-]}{z.A*}\sqrt{\frac{D_A}{D_B}} \tag{2.11}$$

Accordingly, the rate of CO_2 gas absorption into the NaOH solution will follow the equation:

$$R_a = \frac{a.H.pA.\phi\ k_L}{1+\frac{a.H.\phi\ k_L}{k_{GA}}} \tag{2.12}$$

Where Φ is the enhancement factor, which represents the ratio of the CO_2 mass transfer coefficient in the liquid phase when absorption is accompanied by a chemical reaction to that when absorption occurs without a chemical reaction, as formulated by Juvekar and Sharma (1973):

$$\Phi = \frac{\sqrt{D_A.k_{2.}[OH^-]}}{k_L}.\left[\frac{1+\frac{[OH^-]D_B}{z.A*\ D_A}\Phi}{\frac{[OH^-]}{z.A*}.\frac{D_B}{D_A}}\right]^{\frac{1}{2}} \tag{2.13}$$

The effective diffusivity (D_A) of CO_2 in NaOH solution at a temperature of 30 °C is 2.1×10^{-5}cm²/s (Juvekar & Sharma, 1973).

The value of k_{GA} can be calculated based on physical absorption by considering the overall mass transfer of CO_2 into the NaOH solution occurring over a certain time interval in the absorption apparatus. In dimensionless form, k_{GA} can be calculated using the following equation (Kumoro & Hadiyanto, 2000):

$$Sh = a \times Re^b \times Sc^c \tag{2.14}$$

$$\frac{k_{GA}.dp^2}{D_{AB}} = 4{,}0777 \times \left(\frac{\rho_{CO_2}.v.dp}{\mu_{CO_2}}\right)^{1{,}4003} \times \left(\frac{\mu_{CO_2}}{\rho_{CO_2}.D_{AB}}\right)^{\frac{1}{3}} \tag{2.15}$$

$$\frac{k_{GA}.dp^2}{D_{AB}} = 4{,}0777 \times \left(\frac{\rho_{CO_2}.Q.dp}{A.\mu_{CO_2}}\right)^{1{,}4003} \times \left(\frac{\mu_{CO_2}}{\rho_{CO_2}.D_{AB}}\right)^{\frac{1}{3}} \tag{2.16}$$

With $A = \frac{\pi.D^2}{4}$

Theoretically, the value of k_{GA} should satisfy the following equation:

$$k_{GA} = \frac{mol\ (Co_2,liq)}{A.Z.\epsilon\ P_{lm}} = \frac{mol\ (CO_3{}^{2-})}{A.Z.\epsilon\ P_{lm}} \tag{2.17}$$

If the operating pressure is sufficiently low, P_{lm} can be approximated as:

$$\Delta P = P_{in} - P_{out} \tag{2.18}$$

Meanwhile, the value of k_{LA} can be calculated empirically using the following equation (Zheng & Xu, 1992):

$$\frac{k_{LA}.dp}{D_A} = 0{,}2558 \times \left(\frac{\rho_{NaOH}.Q_{NaOH}.4.dp}{\pi.\mu_{NaOH}.D_c{}^2.\varepsilon}\right) \times \left(\frac{\mu_{NaOH}}{\rho.D_A}\right)^{0{,}5} \tag{2.19}$$

If the rate of Na_2CO_3 formation is much greater than the rate of CO_2 diffusion into the NaOH solution, then the concentration of CO_2 at the boundary between the liquid film and the bulk liquid is zero. This is due to the very rapid consumption of CO_2 during the reaction along the film. Therefore, the film thickness (δ) can be determined using the following equation:

$$\delta = \frac{D_A(P_{in}-P_{out})}{mol\ (CO_3{}^{2-}).R.T} \tag{2.20}$$

CHAPTER III

PRACTICUM METHOD

3.1 Trial Design

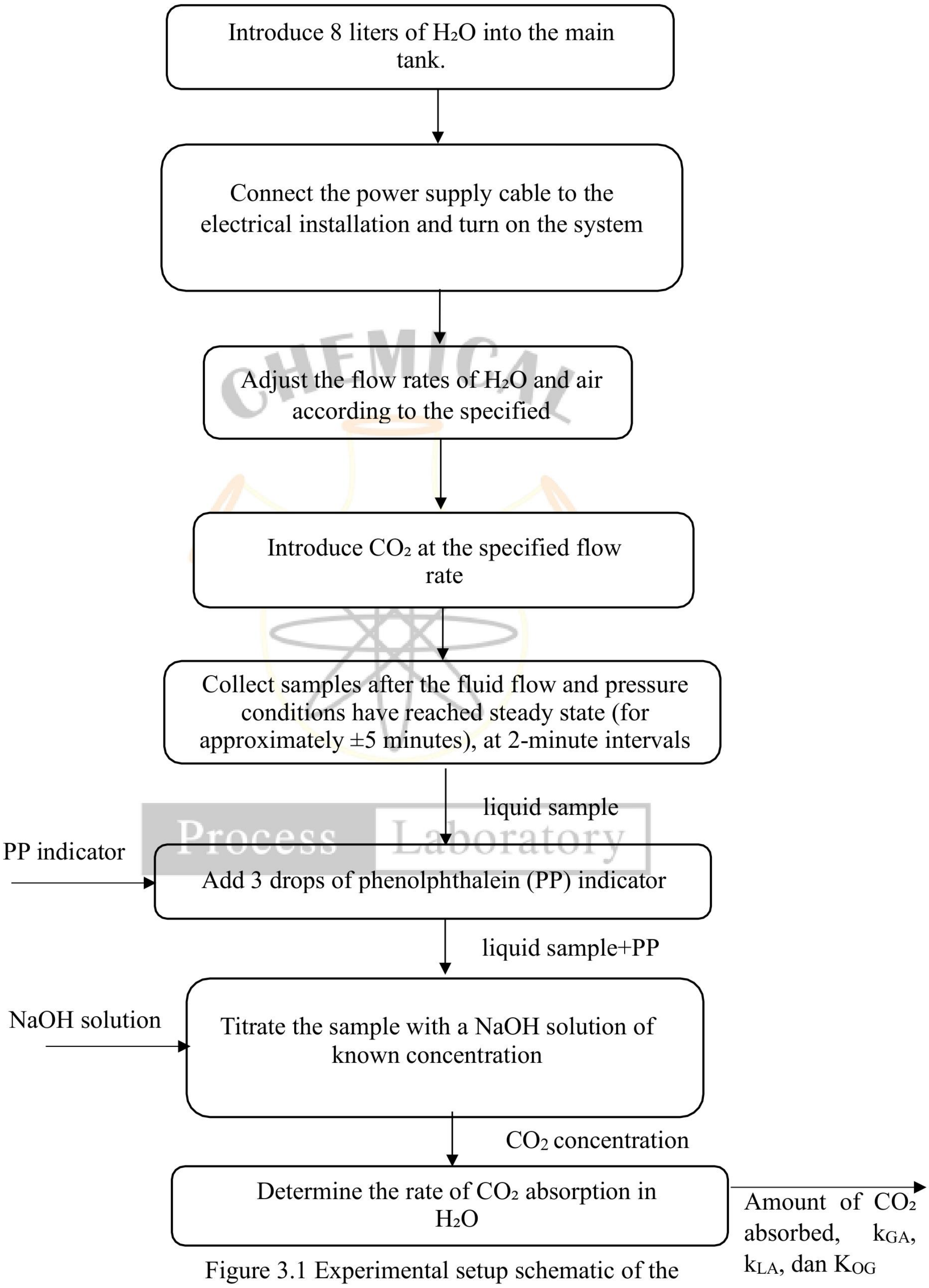

Figure 3.1 Experimental setup schematic of the laboratory experiment

3.1.1 Determination of variables

A. Constant variables:

B. Independent variables:

3.2 Materials and Equipment Used

1. Materials
    1. Sodium hydroxide (NaOH) crystals with a purity of 98% w/w
    2. Carbon dioxide (CO_2) in liquid phase stored in a pressurized cylinder
    3. Air
    4. Aquadest (H_2O)
    5. Phenolphthalein (PP) indicator
2. Equipment

    The experimental absorption apparatus is shown in Figure 3.2.

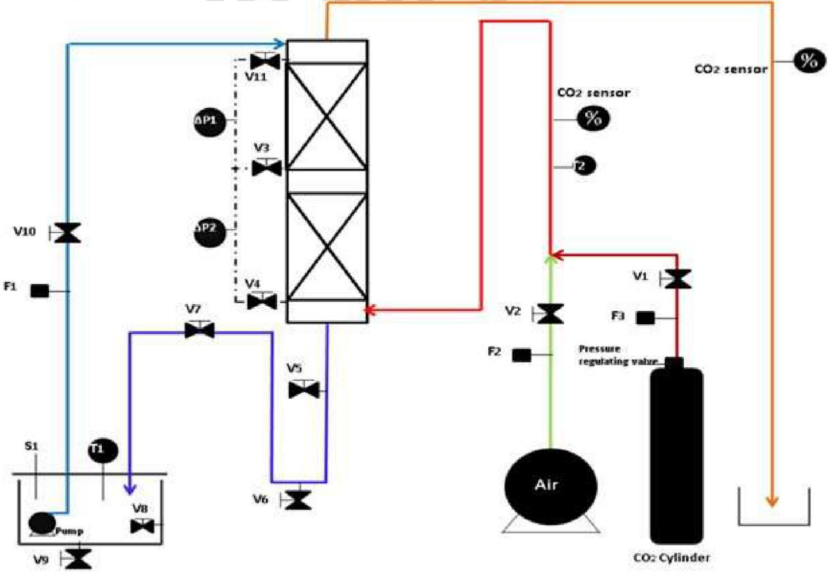

Figure 3.2 Main experimental apparatus setup

3.3 Test Response

Carbonate ion (CO_3^{2-}) concentration in the sample solution and the amount of CO_2 absorbed.

3.4 Experimental Procedure

A. Equipment Preparation

First, the power cable is connected to the electrical power source, followed by turning the ON/OFF switch, and the instrument monitor will turn on. The main water supply to the tank is opened and the tank is allowed to fill. Ensure that the water outlet line from the column is connected to the pipe that returns the water to the tank. With gas flow valves V_1 and V_2 closed, the liquid pump is turned on. The water flow through the column, as indicated by flowmeter F_1, is adjusted using valve V_{10}. The compressor is turned on and valve V_2 is adjusted to provide an air flow. The pressure-regulating valve on the CO_2 cylinder is opened, and valve V_1 is adjusted to set the reading on flowmeter F_3. After 5 minutes (when fluid flow and pressure conditions have reached steady state), 25 mL of liquid sample is withdrawn through the outlet valve at the bottom of the absorber column at 2-minute intervals for 14 minutes, and the pressure difference displayed on the monitor is recorded. The liquid samples are analyzed for dissolved carbon dioxide content in the form of carbonate ions according to the procedure described in Section B.

B. Determination of Dissolved CO_2

Two to three drops of PP indicator are added to the liquid sample. If a red color forms immediately, this indicates the absence of free CO_2 in the sample. The sample is then titrated with a standard NaOH solution according to the specified variables until a pale pink color persists for 30 seconds. The volume of titrant required during the titration is recorded and used to calculate the amount of carbon dioxide dissolved in the sample.

The amount of CO_2 dissolved in the water sample is calculated from:

$$\text{gmol/liter } CO_2 = \frac{V_{\text{titrant}} \times N_{\text{titrant}}}{\text{Sample volume}} = Cd$$

3.5 Observation Sheet

3.5.1 Operating Variables

a. Constant variables:

b. Independent variables:

3.5.2 Data

Table 3.1 Data for variable 1

Time (minutes)	Va out (mL)	ΔP_1	ΔP_2

Table 3.2 Data for variable 2

Time (minutes)	Va out (mL)	ΔP_1	ΔP_2

Table 3.3 Data for variabel 3

Time (minutes)	Va out (mL)	ΔP_1	ΔP_2

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