Work Plan ST8 - Carbon Dioxide Absorption in a Membrane Contactor

Group B5
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1 Introduction

One of the biggest challenges in the world today is the climate crisis, due to the increasing amount of CO_2 in the atmosphere. This leads to air pollution and global warming. Gas-liquid membrane contractors can remove CO_2 from a gas, and is therefore very useful to solve environmental issues [1]. In this experiment, a gas-liquid membrane will be used to remove CO_2, and the absorption rate of CO_2 will be determined as a function of liquid velocity. Lastly, the experimental measurements of the absorption rate will be compared to the theoretical absorption rate that is determined from Fick's first law.

2 Theory

2.1 Membrane Contactor

A membrane contactor is a device used to conduct mass transfer between two phases. Inside the membrane contactor there is a porous membrane, which is used to carry out mass transfer between the two phases without allowing one phase to disperse into the other. [1] The membrane does not work as a selective barrier, and does not control the transport between the phases. Its main function is to keep the phases separated and in contact at the same time. [2]

The selectivity of the process is governed by the difference in the absorbents affinity for the target component. Usually, columns, mixers and towers are used to allow mass transfer between the phases. In these units, the phases are in direct contact with each other, which leads to operational problems such as foaming and flooding. In a membrane contactor, the phases can be controlled separately, which eliminates such problems. [3]

2.2 Theoretical Model for the Absorption Rate

The mass transport through a membrane is a diffusive transport, assuming steady-state conditions, the molar absorption rate can be described using Fick's first law: [1]

$$J_A = -D_A \left(\frac{\partial \mu_A}{\partial x} \right) \tag{2.1}$$

Where J_A is the molar flux of component A across the surface, D_A is the diffusion coefficient, μ_A is the chemical potential and x is the distance. J_A is the same as the absorption rate of component A.

The chemical potential across the interface is a continuous function, to simplify the calculations, the diffusion is split into three parts. From the gas phase onto the membrane surface (phase α), through the membrane, membrane-phase, and from the membrane surface into the liquid bulk (phase β). At steady state, the flux through all phases are equal. By assuming that the diffusion during the phase α and the membrane-phase is much faster than the diffusion during phase β, the flux will be controlled by the absorption of the target component into the liquid phase. Then the flux can be described using equation (2.2) [1]:

$$J_A = k_L \left(C_A^i - C_A^b \right) \tag{2.2}$$

Where k_L is the average liquid phase mass transfer coefficient, C_A^i is the interface concentration as given by Henry's law and C_A^b is the liquid bulk concentration.

The mass transfer coefficient k_L can be determined from the Sherwood number, using equation 2.3:

$$Sh = \frac{k_L d}{D_A} \tag{2.3}$$

Where Sh is the Sherwood number, d is the diameter of the fibers and D_A is the diffusion coefficient. The Sherwood number can be used to describe the ratio between convective and diffusive mass transport. By applying the analogy of Leveque's solution for heat transfer, the Sherwood number can be estimated from Table 2.1 [1].

Table 2.1: Values for estimating the Sherwood number from Graetz number [1]

Graetz number (Gz)	Sherwood number (Sh)
< 10	3.67
$10 < \mathrm{Gz} < 20$	$(3.67^3 + 1.62^3\mathrm{Gz})^{1/3}$
$20 <$	$1.62\mathrm{Gz}^{1/3}$

The Graetz number, Gz, is defined by equation (2.4):

$$G_z = \frac{v_L d^2}{D_A L} \tag{2.4}$$

Where v_L is the velocity of the liquid, and L is the length of the fiber.

By assuming that the liquid flow in the fibers are laminar, and that the velocity profile is fully developed, the liquid bulk concentration, at any axial distance z, can be calculated using equation (2.5) [1].

$$C_A^b|_z = C_A^i \left[1 - exp\left(-\frac{4k_L z}{v_L d}\right)\right] \tag{2.5}$$

The average liquid bulk concentration in the fiber, which will be used in equation (2.2), can be found by taking integrating C_A^b over the length of the fiber:

$$\langle C_A^b \rangle = \frac{1}{L}\int_0^L C_A^b dz \tag{2.6}$$

Inserting the expression for C_A^b from equation (2.5) into equation (2.6), and integrating, finally gives the expression for the liquid bulk concentration in the fibers.

$$C_A^b = \frac{C_A^i}{L}\left[L + \frac{v_L d}{4k_L}\exp\left(-\frac{4k_L L}{v_L d}\right) - \frac{v_L d}{4k_L}\right] \tag{2.7}$$

The interface concentration, C_A^i, used in equations (2.2) and (2.7), can be found using Henry's law [4]:

$$C_A^i = K_A P_A \tag{2.8}$$

K_A is the Henry's law constant of component A and P_A is the partial pressure.

Equation (2.2) is only valid when the gas-liquid interface conditions are constant, which is not the case in this experiment. For high partial pressures of CO_2, the absorption rate will be high, which will lead to a decrease in both pressure, and partial pressure. This causes a lower concentration of CO_2 in the gas-liquid interface. For this reason, large deviations are to be expected between the theoretical model and the experimental results, especially at high liquid flow rates [1].

2.3 The First Humidifier

The first humidifier adds water vapor to the gas inlet. This is to make sure that the partial water vapor is higher or equal to the total vapor pressure. The reason why this step is important is because liquid phase water will not go into the pores in the membrane (this is called wetting). Wetting will increase the mass transfer coefficient. This means that a higher amount of gas is able to pass through the membrane. [5]

2.4 BTB

BTB (Bromothymol blue) is an indicator which indicates the pH of the solution. When the pH is under 6.8, the solution is yellow, and at pH over 6.8 the solution will be blue if BTB is in the solution. [6]

In this experiment, the reaction will occur:

$$CO_2 + H_2O \rightleftharpoons HCO_3{}^- + H^+ \tag{2.9}$$

When the CO_2 is absorbed, the water will become more acidic. When this happens, the BTB will change the color from blue to yellow. Since the experiment happens at a close-to neutral pH, BTB is a good choice of indicator, and the change from blue to yellow will be clear.

3 Experimental Procedure

3.1 Apparatus

The experiment will be performed in a membrane contactor rig, where a mixture of N_2 and CO_2 will be brought into indirect contact with a mixture of distilled water, 0.01 M NaOH and BTB indicator. Two parallel membrane contactors coupled in parallel are used in order to increase the absorption capacity [1]. The experimental set-up is shown in Figure 3.1. Physical parameters for the set-up can be found on data sheets in the lab.

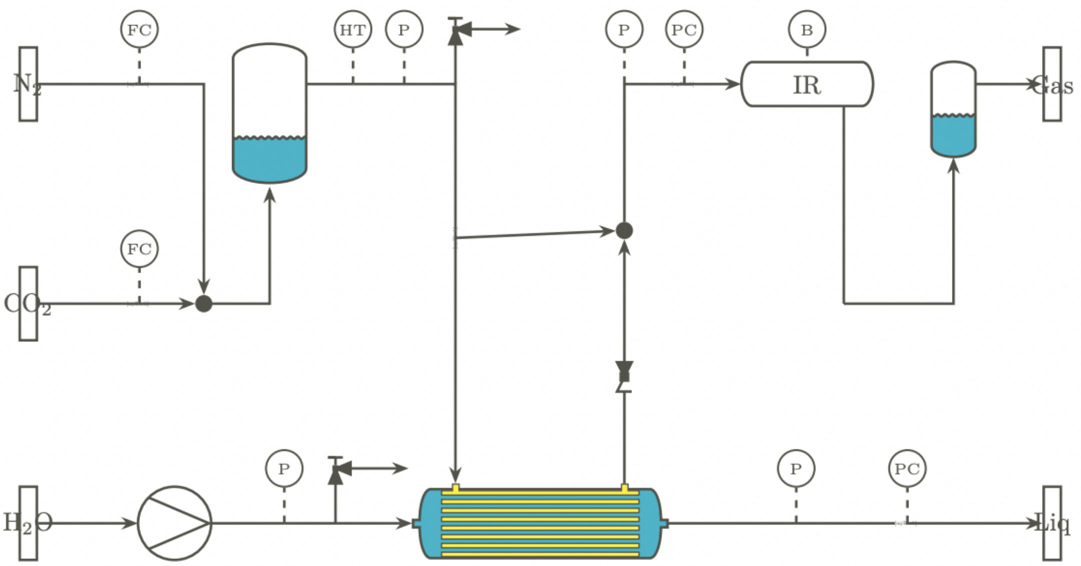

Figure 3.1: The experimental setup for the membrane contactor rig [1]. F stands for flow, H for humidity, P for pressure, T for temperature and C for control.

3.2 Execution

The experiment will be performed using the following procedure [1]:

1. Add 25 L of distilled water and a small amount of BTB, bromothymol blue, to the feeding tank.
2. To get a pH of 7.5, add 0.79 mL of 0.01 M NaOH to the feeding tank. The calculation of the necessary amount of NaOH solution is presented in Appendix A.1.
3. Enter the preselected set-points into the controllers. The set-points are presented in Table 3.1.
4. Calibrate the IR-sensor using the following procedure
   (a) Bypass the membrane contactor unit by using the 3-way valve.
   (b) Set the controls to the set-points.
   (c) When the 16-bit number stabilizes, write it down.
   (d) Lower the amount of CO_2, by using a lower set-point for the flow controller. Increase the amount of N_2 so the total amount of gas in the system i constant. Repeat the steps above for the different set-points presented in Table 3.2.
   (e) Using the code in Appendix B.1, make a linear regression. Using the 16-bit number as the x-value, and the percentage of CO_2 in the flow as the y-value. Enter the result into the software.
   (f) Reset the controllers to the initial set-point values, and lead the gas flow into the membrane unit using the 3-way valve.
5. At a low pump velocity, pump the feeding water into the lumen of hollow fibers. Ensure that the is no air in the liquid feeding hos before proceding to the next step.
6. When the concentration of CO_2 stabilizes, measure the necessary time it takes to collect a given amount of liquid. This is done using a measuring cylinder and a stop watch.
7. In order to measure other necessary variables, press *'Start'* in the software. Stop the measuring by pressing *'Stop sampling'*.
8. Repeat the two previous steps for increased pump rates. In total, the experiment should be run for 10 different pump flow rates.
9. Reset all the controllers, transfer the collected data to a USB-stick and clean up.

Table 3.1: Set-points for the membrane contactor rig. psia is absolute pressure, and psig is relative pressure.

Controller	Description	Set-point	Units
CO_2	Flow controller for pure CO_2 in	0.25	$\mathrm{L\,min^{-1}}$ (STP)
N_2	Flow controller for pure N_2 in	0.25	$\mathrm{L\,min^{-1}}$ (STP)
P_g	Pressure controller for the gas outlet	17	psia
P_l	Pressure controller for the liquid outlet	17	psig

Table 3.2: Set-points used during the calibration of the IR-sensor

Flow rate CO_2 $[\mathrm{L\,min^{-1}}]$	Flow rate N_2 $[\mathrm{L\,min^{-1}}]$	% CO_2 in the gas phase
0.10	0.40	20
0.15	0.35	30
0.20	0.30	40

3.3 Data and Measurements to Be Taken

The following data needs to be written down during the experiment:

- 16-bit numbers from IR-calibration.
- Parameters from the linear regression during the IR-calibration.
- Liquid flow rate, q_L, calculated from the the time required to fill a cylinder of a known volume.
- Length of the fibers, L
- Diameter of the membrane fibers (inner), d

The following data will be measured by the software:

- Temperature of the gases, T
- Flow rates of the gases, $q_{\mathrm{CO_2}}$ and $q_{\mathrm{N_2}}$
- Pressures for the gas inlets and outlets.
- Pressures for the liquid inlet and outlet.
- Composition of the gas through outlet, $y_{\mathrm{CO_2}}$

4 Health, Safety and Environment

This is a relatively safe experiment, but there are some possible risks. Exposure to BTB over time can cause eye irritation or lung damage. If it is spilled on the skin or eyes, rinse with large quantities of water. NaOH can be spilled, CO_2 can leak and equipment breakage (cuts etc.). NaOH can cause blindness if it is in contact with eyes and it can cause burning damage on the skin. Due to this, spill of NaOH is the biggest risk in this experiment. It is a low concentration, but to prevent a dangerous situation, using protective gloves will lower the risk. Lab coat and glasses is always mandatory in the lab.

The COVID-19 restrictions has been repealed, so it is not necessary to do much due to infection control. As a precaution, the lab space and equipment used during the experiment should be wiped before leaving the lab.

Trondheim, January 9, 2022

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A Calculations

A.1 Preparing the Feed Tank Solution

The feeding tank is to be filled with 25 L of a solution with a pH of 7.5. This is to be achieved by adding an amount of 0.01 M NaOH. In water, NaOH dissolves by the following reaction:

$$\mathrm{NaOH(aq)} \longrightarrow \mathrm{Na^{+}(aq)} + \mathrm{OH{-}(aq)} \tag{A.1}$$

NaOH is a strong base, and is assumed to dissolve completely. As pH is dependent on the concentration of H^{+}, it is more convenient to use pOH. The relation between pH and pOH is given by,

$$\mathrm{pH} + \mathrm{pOH} = 14 \tag{A.2}$$

Which gives pOH = 6.5. pOH can be defined by this expression [7]:

$$\mathrm{pOH} = -\log{[\mathrm{OH^{-}}]} \tag{A.3}$$

Rearranging equation (A.3), the necessary concentration of OH^{-} in the solution can be found:

$$c_{\mathrm{OH^{-}}} = 10^{-\mathrm{pOH}} = 3.163 \cdot 10^{-7} [\mathrm{mol\,L^{-1}}] \tag{A.4}$$

From reaction (A.1), the number of moles of NaOH needed in the mixture is equal to the number of moles of OH^{-}. This can be calculated using,

$$n_{\mathrm{NaOH}} = n_{\mathrm{OH^{-}}} = c_{\mathrm{OH^{-}}} \cdot V = 3.163 \cdot 10^{-7} \mathrm{mol\,L^{-1}} \cdot 25\,\mathrm{L} = 7.905 \cdot 10^{-6}\,\mathrm{mol} \tag{A.5}$$

The necessary amount of 0.01 M NaOH can then be found,

$$V_{\mathrm{ceNaOH}} = \frac{n_{\mathrm{NaOH}}}{c_{\mathrm{NaOH}}} = \frac{7.905 \cdot 10^{-6}\,\mathrm{mol}}{0.01\,\mathrm{mol\,L^{-1}}} = 0.79\,\mathrm{mL} \tag{A.6}$$

To make a 25 L solution with a pH of 7.5, 0.79 mL of 0.01 M NaOH solution needs to be added to the feeding tank.

A.2 Determining the Absorption Rate

To determine the absorption rate, the following equations need to be used:

$$J_{\mathrm{CO_2,exp}} = \frac{n_{\mathrm{CO_2,in}} - x_{\mathrm{CO_2,out}}}{1 - x_{\mathrm{CO_2,out}}} \tag{A.7}$$

$$n_{\mathrm{CO_2},out} = \frac{y_{\mathrm{CO_2,out}} n_{\mathrm{N_2}}}{1 - y_{\mathrm{CO_2,out}}} \tag{A.8}$$

where

$$n_{\mathrm{N_2}} = n_{\mathrm{CO_2,in}}$$

and

$$y_{\mathrm{CO_2,out}} = \frac{n_{\mathrm{CO_2,out}}}{n_{\mathrm{CO_2,out}} + n_{\mathrm{N_2}}}$$

The theoretical absorption is found by using equations (2.2), (2.4) and (2.8). k_L is found by using equation (2.3), and v_L is calculated from:

$$v_L = \frac{q_L}{A_{\text{fiber cross section}} N_{\text{fiber}}} \tag{A.9}$$

B Python Code

B.1 Calibrating the IR-sensor - Linear Regression

Below is the code that will be used to get parameters to calibrate the IR-sensor.

```
import numpy as np
import matplotlib.pyplot as plt


ir_values, percentageCO2 = np.loadtxt("IR-data.txt", usecols=(0, 1),
                                      skiprows=1, unpack=True)
params, cov = np.polyfit(ir_values, percentageCO2, 1, cov=True)
f = np.poly1d(params)
x_values = np.linspace(0,ir_values[-1], 100)
plt.plot(x_values, f(x_values), label="Regression line", color="grey")
plt.scatter(ir_values, percentageCO2, label="Datapoints", color="black")
plt.xlabel(r"$IR-value$")
plt.ylabel(r"%CO$_2$")
plt.legend()
plt.show()

print(f"a = {params[0]:.5f}")
print(f"b = {params[1]:.5f}")
```