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# CFD Modelling of a Hollow Fibre Membrane for CO<sub>2</sub> Removal by Aqueous Amine Solutions of MEA, DEA and MDEA

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**Abstract:** A mass transfer model was developed to capture CO<sub>2</sub> from a gas mixture in hollow fibre membrane contactors under laminar flow conditions. The axial and radial diffusions through membrane and convection in tube and shell sides with chemical reaction were investigated. COMSOL software was used to numerically solve a system of non-linear equations with boundary conditions by use of the finite element method. Three different amine solutions of monoethanolamine (MEA), diethanolamine (DEA) and *n*-methyldiethanolamine (MDEA) were chosen as absorbent in lumen to consider the mass transfer rate of CO<sub>2</sub> and its removal efficiency. The modelling results were compared with experimental data available in the literature and a good agreement was observed. The CFD results revealed that MEA had the best performance for CO2 removal as compared to DEA and MDEA under various operating conditions due to the different CO2 loading factor of absorbents. Furthermore, efficiency of CO<sub>2</sub> removal was highly dependent on the absorbent concentration and flow rate, increasing of the gas flow rate caused a reduction in gas residence time in the shell and consequently declined CO2 mass transfer. The modelling results showed the effect of absorbent concentration on the CO<sub>2</sub> mass transfer was improved due to availability of absorbent reactants at the gas-liquid interface.

**Keywords:** amine solutions, CFD modelling, CO<sub>2</sub> separation, hollow fibre membrane

### 1 Introduction

One of the most current controversial topics is the effect of greenhouse gases on the environment which causes climate change and global warming. The  $\rm CO_2$  emission

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from the combustion of fossil fuels is regarded as the main contributor to the enhancement of the greenhouse effect (Halmann and Steinberg 1998). Nowadays, scientists and researchers are highly focusing on devising and improving efficient methods for mitigating  $\rm CO_2$  generated by industry and power plants (Casper 2010). As  $\rm CO_2$  constitutes a main part of flue gas and 80% of greenhouse gases, its removal by use of absorption, adsorption and membrane methods can considerably reduce and control the risk of emission problems.

The conventional separation methods for CO2 capture based on amine absorbents are still in use, although the regeneration process is highly energy intensive and causes operational problems such as flooding and foaming (Moulijn, Makkee, and Van Diepen 2013). The commonly used absorbents are aqueous solutions of alkanolamine such as MEA, DEA and MDEA which are still used in packed columns for CO<sub>2</sub> removal (Veawab, Aroonwilas, and Tontiwachwuthikul 2002). The performance of these solutions was experimentally evaluated in an absorber column and revealed that MEA had the best CO2 removal efficiency amongst DEA and MDEA solutions (Aroonwilas and Veawab 2004). By the advent of industrial membrane technology in 1980 (Baker 2012), scientists and engineers gave their attention to utilize different types of polymeric membranes in spiral-wound and hollow fibre modules. Cynara (USA) and Separex (France) were two major companies which fabricated the system for separation of CO<sub>2</sub> from natural gas (Baker 2012). The gas-liquid hollow fibre membrane contactor is a substantial candidate to be replaced with conventional systems in which a similar mechanism of mass transfer exists between two phases and also the rate of CO2 absorption significantly undergoes the use of various absorbents (Li and Chen 2005). Due to the hydrophobic properties of polymeric membranes in gas separation, a solid barrier is made to impede the penetration of liquid phase into the gas phase. Instead, the gas phase completely fills the membrane pore channels and forms a gas-liquid interface. Therefore, gas diffusion occurs on account of the difference in concentration of the absorbent type more than the pressure gradient (Mansourizadeh and Ismail 2007). In terms of membrane material selection, the hollow fiber modules are mainly dependent on the  $\rm CO_2$  reactivity of absorbent rather than the flat sheet modules which need a treatment method in order to alter the morphology of the polymeric membrane and enhance the separation efficiency. In this way, the measurement of permeability and selectivity of a membrane can partially simplify selection of an appropriate polymeric for a gas separation system (Gilassi and Rahmanian).

Mass transfer in hollow fibre membranes is highly dependent on the overall mass transfer which includes three individual mass transfer coefficients relating to the liquid phase, membrane, and gas phase boundary layer (Zhang and Wang 2013). The effect of partial or wetted pores on membrane mass transfer coefficient is to cause an increment because of the stagnant liquid phase in pore channels (Rangwala 1996). Mansourizadeh and Ismail (2007) studied the effect of liquid temperature and pressure on the absorption/stripping of CO<sub>2</sub>/N<sub>2</sub> gas mixture by developing hydrophobic polyvinylidenefluoride (PVDF) hollow fibre membranes. Yang et al. (2012) investigated the efficiency of CO<sub>2</sub> removal by polypropylene (PP) hollow fibre membranes with MEA as the absorbent for removal of SO2 content in the flue gas of power plants. They showed a good affinity between amine absorbent and sulphuric gas to remove both CO<sub>2</sub> and SO<sub>2</sub> spontaneously. Similarly, Hedayat et al. (2011) conducted removal of CO2 and H2S from a gas mixture similar to natural gas in PVDF and polysulfone (PSF) hollow fibre membranes simultaneously. Simulation of the CO<sub>2</sub> removal system is a valid method to optimize the separation by the change in operating variables such as gas and liquid velocity, membrane pressure drop and temperature for one or multi-stage separation systems. Diverse models relating to transport equations with specific model assumptions have been suggested to predict the concentration of CO<sub>2</sub> absorption in HFMCs using different absorbents. Zhang et al. (2006) presented a model to indicate the effect of increase in liquid flow rate on the CO<sub>2</sub> flux with distilled water and aqueous DEA as solvents whilst axial diffusion was neglected. They concluded that the physical reaction of CO<sub>2</sub> with distilled water had been less effective than the chemical reaction of CO<sub>2</sub> with MEA. The model by Razavi et al. (2013) showed the influence of absorbent flow rate on the efficiency of CO<sub>2</sub> removal based on the assumption that the velocity at the surface of the membrane was non-slip. Gilassi and Rahmanian (2014) developed a mathematical

model to predict the CO<sub>2</sub> concentration in a flat sheet module for CO<sub>2</sub>/CH<sub>4</sub> separation and also investigated the effect of slip boundary condition at the membrane interface. The modelling result revealed that the slip condiwas highly dependent on the membrane permeability and an empirical factor which caused the fluid reflection at the gas-membrane interface. The results revealed that the mass transfer model had been more accurate than the conventional model without chemical reaction. Saidi et al. (2014) developed a model to investigate the effect of DEA, MDEA and the blend of these solutions on the CO<sub>2</sub> capture. Their results showed that DEA solution was the best performance for CO2 removal amongst the other solutions. In terms of model development, a numerical comparison between one and two dimensional models for CO<sub>2</sub> capture with MEA solution using a hollow fiber membrane was also presented by Albarracin Zaidiza et al. (2014) to examine the accuracy of developed models. Use of various absorbents has different influences on the CO2 removal efficiency and absorbent selection is likely regarded as important criteria to optimize a separation process (Kothandaraman et al. 2009).

In this study, a two-dimensional model of mass transfer is presented to highlight the effect of absorbent type and flow rate on CO<sub>2</sub> concentration in a hollow fibre membrane contactor. COMSOL software was used to solve continuity and momentum equations regarding the boundary conditions at the interface of three phases. The presented model simulates the radial and axial diffusions through the membrane and convection inside shell and tube of module. This study also considers the effect of chemical reaction on the tube side between CO2 and amine solutions of MEA, DEA and MDEA and therefore the modelling result can be confidently used to simplify the selection of efficient absorbent amongst the amine solutions. Figure 1 shows a schematic plan of a hollow fibre membrane contactor. In order to validate the model, the modelling result is compared with experimental data obtained from the literature (Yan et al. 2007).

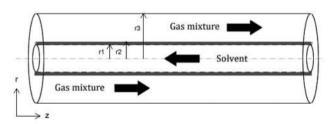


Figure 1: Schematic plan of a hollow fibre mebrane contactor.

# 2 Model development

A two-dimensional mass transfer model is proposed for CO<sub>2</sub> capture from a gas mixture of CO<sub>2</sub>/N<sub>2</sub> in a hollow fibre membrane contactor. The separation is followed by a chemical reaction between the gas and liquid phases. The model is based on "non-wetting mode" so that the pore channel of the membrane is filled by the gas phase. The gas phase flows inside the shell whereas the liquid phase flows inside the tube in counter-current mode. Table 1 shows the HFMC details (Faiz and Al-Marzougi 2009), and the model pursues the assumption as follows:

- Gas and liquid flows are in steady-state and isothermal conditions.
- Gas flow conforms to Happel's free surface model (Happel 1959) and ideal gas law.
- Equilibrium between gas-liquid phases is determined by Henry's law.
- Non-slip conditions at the membrane surface and fully developed velocity profile were seen.

Table 1: Dimension of hollow fibre membrane contactor (Faiz and Al-Marzougi 2009).

Parameter	Values
Inner radius of tube (mm)	0.22
Outer radius of tube (mm)	0.30
Inner radius of shell (mm)	0.529
Membrane length (cm)	22
Number of fibres (-)	3600
Porosity (%)	40
Tortuosity (–)	2

#### 2.1 Shell equations

Generally, the Navier-Stokes equations determine the velocity in the shell side for incompressible fluid and can be written as follows:

$$\frac{\partial u}{\partial t} + (u \cdot \nabla)u = -\nabla p + v\Delta u \tag{1}$$

$$\nabla . u = 0 \tag{2}$$

where u (m/s) is velocity vector in the r and z directions, p (Pa) and  $\nu$  (cP) are pressure and viscosity, respectively. The effective radius is specified according to Happel's model (1959) and expressed as follows:

$$r_3 = \left(\frac{1}{1 - \phi}\right)^{1/2} r_2 \tag{3}$$

$$1 - \phi = \frac{m_2^2}{R^2} \tag{4}$$

where u,  $r_3$ ,  $r_2$  denotes the average velocity (m/s) radius of free surface (m) and fibre outer radius (m), respectively. R is the module inner radius (m),  $\phi$  is the volume fraction of the void, and n is the number of fibres. The continuity equation containing diffusion and convection in cylindrical co-ordinates can be expressed as follows (Bird, Stewart, and Lightfoot 2007):

$$D_{shell}\left(\frac{\partial^{2}C_{CO_{2}}}{\partial r^{2}} + \frac{1}{r}\frac{\partial C_{CO_{2}}}{\partial r} + \frac{\partial^{2}C_{CO_{2}}}{\partial z^{2}}\right) = u_{z}\frac{\partial C_{CO_{2}}}{\partial z}$$
(5)

where C (mol/m<sup>3</sup>) denotes the concentration. The diffusivity coefficient D (m<sup>2</sup>/s) is determined using the Chapman-Enskog theory (Mills 2001). Boundary conditions are expressed as follows:

$$z = L \quad C_{shell} = C_0 \tag{6}$$

$$r = r_3 \frac{\partial C_{shell}}{\partial r} = 0$$
 (7)

$$r = r_2$$
  $C_{shell} = C_{membrane}$  (8)

#### 2.2 Membrane equations

The transport equation inside the membrane, which predicts CO<sub>2</sub> concentration, has only a diffusion term under steady-state conditions as follows:

$$D_{membrane} \left( \frac{\partial^2 C_{CO_2}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{CO_2}}{\partial r} + \frac{\partial^2 C_{CO_2}}{\partial z^2} \right) = 0$$
 (9)

Diffusivity coefficient in membrane,  $D_{membrane}$  (m<sup>2</sup>/s), can be calculated by eq. (10) (Al-Marzougi et al. 2008).

$$D_{membrane} = D_{shell} \frac{\varepsilon}{\tau} \tag{10}$$

where  $\varepsilon$  and  $\tau$  are porosity and tortuosity, respectively. Boundary conditions are defined as follows:

$$r = r_2$$
  $C_{membrane} = C_{shell}$  (11)

$$r = r_1 \quad C_{membrane} = C_{tube}/H$$
 (12)

where H is a dimensionless parameter, i.e. Henry's coefficient.

#### 2.3 Tube equations

The continuity equation with a chemical reaction term is given by eq. (12).

$$D_{tube}\left(\frac{\partial^2 C_{CO_2}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{CO_2}}{\partial r} + \frac{\partial^2 C_{CO_2}}{\partial z^2}\right) = u_z \frac{\partial C_{CO_2}}{\partial z} + R_i$$
 (13)

where  $R_i$  (mol/m<sup>3</sup>s) is the reaction rate of CO<sub>2</sub> and  $D_{tube}$ (m<sup>2</sup>/s) is diffusivity coefficient in tube which can be calculated from N<sub>2</sub>O analogy (Versteeg and Van Swaali 1988). The boundary conditions are expressed as follows:

$$z = 0$$
  $C_{tube} = 0$ ,  $C_{absorbent} = C_{absorbent-in}$  (14)

$$r = r_1 \quad C_{tube} = C_{membrane} \times H$$
 (15)

$$r = 0 \quad \frac{\partial C_{tube}}{\partial r} = 0 \tag{16}$$

# 2.4 Reaction rate of CO<sub>2</sub> in amine solution

The reaction between CO<sub>2</sub> with amine solution involves the formation of carbamate, bicarbonate and carbamate reversion (Sakwattanapong, Aroonwilas, and Veawab 2009). The formation is expressed by the zwitterion mechanism as follows:

$$CO_2 + RR'NH \xrightarrow{k_2} RR'NH + COO^-$$
 (17)

$$RR'NH^+COO^- + B \xrightarrow{k_B} BH^+ + RR'NCOO^-$$
 (18)

where R and R' represent  $C_2H_4OH$ , H and  $C_2H_4OH$  for primary and secondary amines, respectively. The rate of reaction of the CO2-MEA and CO2-DEA systems are similarly shown by eq. (18) and for CO<sub>2</sub>-MDEA is expressed by eq. (19). The kinetic constants for MEA-H<sub>2</sub>O solution are given in Table 2 (Paul, Ghoshal, and Mandal 2008).

$$r_{CO_2-MEA} = \frac{k_{2-MEA}[CO_2][MEA]}{1 + 1/(k_{H_2O}/(k_{-1})C_{H_2O}) + (k_{MEA})/(k_{-1})C_{MEA}}$$
(19)

$$r_{CO_2 - MDEA} = k_{2 - MDEA}[CO_2][MDEA]$$
 (20)

Table 2: Kinetic parameters at 298°K (Paul et al. 2008).

Amine aqueous solution	k <sub>2-amine</sub> (m³ mol <sup>-1</sup> s¹)	$k_{2-amine}k_{H_2O}/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )	$k_{2-amine}k_{amine}/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )
MEA + H <sub>2</sub> O	6.35	$9.58 \times 10^{-6}$	$1.58 \times 10^{-3}$
DEA + H <sub>2</sub> O	2.375	$2.20 \times 10^{-6}$	$0.43 \times 10^{-3}$
MDEA + H <sub>2</sub> O	5.21		

#### 3 Numerical scheme

Due to the non-linear form of equations in the suggested model, COMSOL software (ver. 4.3) was chosen to solve the equations numerically with stiff and nonstiff boundary value conditions on the basis of the finite element method. Triangular mesh type with specific size was chosen to discretize the domain and the scale factor is taken into account because of different size length and diameter of fibres. The PARDISO mode (a solver for symmetric and non-symmetric linear systems of equations) was chosen due to non-linearity of the system of equations with the minimum and maximum damping factor of  $1 \times 10^{-4}$  and  $1 \times 10^{-8}$ , respectively.

## 4 Model validation

The mass transfer model is validated by experimental data from the literature (Yan et al. 2007) for CO2 removal with MEA in a hollow fibre membrane. The result of the model presented, including MEA, DEA and MDEA need to be compared with real data. As there is no available experimental data for DEA, therefore the validation is carried out only for MEA. Figures 2 and 3 show the model results which are in good agreement with the reported data. Moreover, the deviation between experimental and modelling results for the effect of liquid and gas flow rates on CO2 mass transfer rate based on the average absolute relative error (ARRE) calculation method, are 0.75% and 8.75%, respectively.

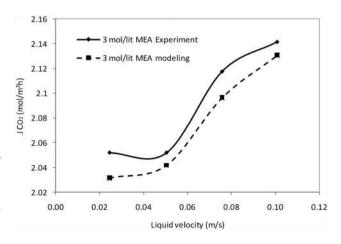


Figure 2: The effect of liquid velocity on CO2 mass transfer rate for MEA solution.

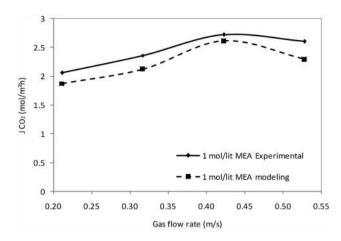


Figure 3: The effect of gas flow rate on CO<sub>2</sub> mass transfer rate for MEA solution.

#### 5 Results and discussion

## 5.1 Velocity profile

The velocity distribution of the gas feed in the shell side is shown in Figure 4. The velocity profile is determined by solving the Navier-Stokes equations with boundary conditions at the walls and membrane surface. The pressure drop along the side of the shell was theoretically estimated by the Hagen-Poiseuille equation (Chang et al. 1998) which was considered to be approximately zero. Furthermore, the velocity near the shell side and membrane surfaces was assumed to be in an identical state which resulted in a symmetric parabolic profile, and consequently, a fully developed profile approximately at the end of the shell appears. It is worthy to mention that the velocity profile at the membrane surface varied regarding membrane structure and permeability (Nield 2009).

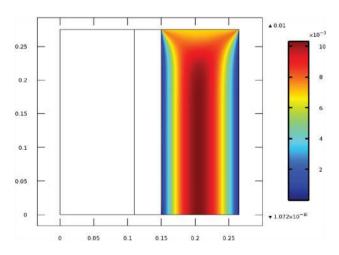


Figure 4: Velocity profile of gas feed in shell.

#### 5.2 Effect of CO<sub>2</sub> concentration

The effect of CO<sub>2</sub> volumetric concentration in the gas feed mixture on the CO<sub>2</sub> mass transfer rate is shown in Figure 5. Based on the transport phenomena in the shell, there has been competition between the components of the gas mixture (N<sub>2</sub>/CO<sub>2</sub>) pertaining to diffusive and convective transfers. Moreover, the CO<sub>2</sub> concentration at the inlet is at its maximum and the concentration at the outlet is the minimum which is independent of diffusion. An increase in CO<sub>2</sub> concentration of gas feed causes the mass transfer rate to decrease for the three amine solutions on condition that the absorbents concentration is 3 mol/litre and gas and liquid velocity are set at minimum value. In this state, MEA shows better CO<sub>2</sub> removal performance than DEA. The MEA curve declines more slightly and thus displays high CO<sub>2</sub> loading property of that amine solution. The sharp slope of the DEA curve represents the high dependency on CO<sub>2</sub> concentration; the descending state can be halted by increasing the absorbent concentration in the tube side. It can be emphasised that the influence of MDEA solution is not shown in Figure 5 owing to the descriptive difference amongst the solution's curves. It is expected to compare the effect of MEA and DEA solutions separately with great accuracy. Moreover, in comparison with three types of amine solution, MEA and DEA have shown considerably better performance than MDEA.

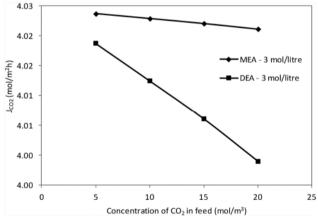


Figure 5: The effect of  $CO_2$  concentration in feed gas on  $CO_2$  mass transfer rate; Liquid velocity = 1.5 m/s, gas velocity = 5.5 m/s, gas pressure = 121.3 kPa and gas temperature = 298°K.

#### 5.3 Effect of absorbent concentration

Figure 6 demonstrates the effect of absorbent concentration on the CO<sub>2</sub> mass transfer rate. An increase in concentration of the three amine solutions resulted in an increase

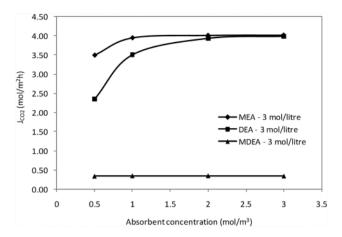


Figure 6: The effect of absorbent concentration on  $CO_2$  mass transfer rate for different amines; Liquid velocity = 1.5 m/s, gas velocity = 5.5 m/s,  $CO_2$  concentration = 20 % vol., gas pressure = 121.3 kPa and gas temperature = 298°K.

of absorbent viscosity. Consequently, they can form a better reaction site at the gas-liquid interface and the CO<sub>2</sub> solubility significantly improves. In this case, the mass transfer rate increases swiftly for DEA solution rather than others while the CO2 concentration of gas feed is at maximum value. In the present modelling, the concentration of CO<sub>2</sub> inside the shell, membrane and tube has been illustrated in Figure 7(a), 7(b), 7(c) for MEA, DEA and MDEA, respectively. CFD Simulation results illustrate the dimensionless concentration of CO<sub>2</sub> for all three types of amine solution in the shell in which a diverse gradient of concentration forms with respect to the absorbent capacity. It is evident that the performance of MEA is noticeably better than MDEA and DEA. MDEA cannot be a proper absorbent while the CO2 concentration of gas feed increases. Figure 8 displays distribution of the absorbent (MEA) inside the tube. As it is expected, CO<sub>2</sub> component of the diffusive gas reacts with the MEA solution at the gasliquid interface. In this way, CFD results show the depletion of the absorbent inside the tube where the MEA

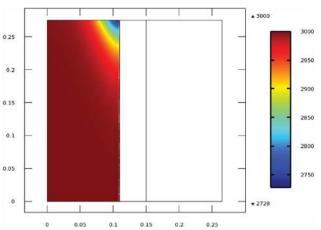


Figure 8: Concentration of MEA in HFMC,  $C_{MEA} = 3 \text{ mol/m}^3$ ,  $C_{CO2} = 20 \% \text{ vol.}$ ,  $U_g = 5.5 \text{ m/s}$ ,  $U_l = 1.5 \text{ m/s}$ .

concentration profile changes at the outlet region due to the high  $\mathrm{CO}_2$  concentration diffused from the inlet of shell side. On the contrary, as the  $\mathrm{CO}_2$  concentration reduces throughout the shell, the reaction between  $\mathrm{CO}_2$  and absorbent at the inlet region of tube is less efficient than the outlet region of tube due to low  $\mathrm{CO}_2$  concentration.

#### 5.4 Effect of gas and liquid flow rates

As the  $\mathrm{CO}_2$  removal efficiency is strongly dependent on the reaction between the gas and liquid phases, it is necessary to increase both gas residence time and absorbent availability at reaction active site in order to produce a more efficient reaction. It is evident that gas flow rate determines the gas residence time in the shell side and similarly through the membrane. Figure 9 shows the effect of gas velocity on  $\mathrm{CO}_2$  mass transfer rate. As it is seen, there are distinctive differences between the three curves of MEA, DEA and MDEA which corresponds to the performance of each absorbent to eliminate  $\mathrm{CO}_2$  and the

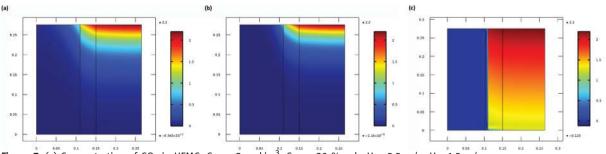


Figure 7: (a) Concentration of CO<sub>2</sub> in HFMC,  $C_{DEA} = 3 \text{ mol/m}^3$ ,  $C_{CO2} = 20 \text{ % vol.}$ ,  $U_g = 5.5 \text{ m/s}$ ,  $U_l = 1.5 \text{ m/s}$ . (b) Concentration of CO<sub>2</sub> in HFMC,  $C_{MEA} = 3 \text{ mol/m}^3$ ,  $C_{CO2} = 20 \text{ % vol.}$ ,  $U_g = 5.5 \text{ m/s}$ ,  $U_l = 1.5 \text{ m/s}$ . (c) Concentration of CO<sub>2</sub> in HFMC,  $C_{MDEA} = 3 \text{ mol/m}^3$ ,  $C_{CO2} = 20 \text{ % vol.}$ ,  $U_g = 5.5 \text{ m/s}$ ,  $U_l = 1.5 \text{ m/s}$ . (c) Concentration of CO<sub>2</sub> in HFMC,  $C_{MDEA} = 3 \text{ mol/m}^3$ ,  $C_{CO2} = 20 \text{ % vol.}$ 

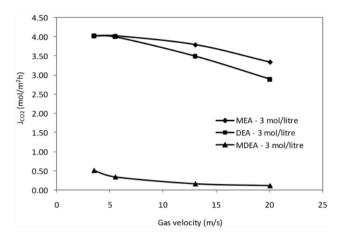


Figure 9: The effect of gas velocity on  $CO_2$  mass transfer rate; Liquid velocity = 1.5 m/s,  $CO_2$  concentration = 20 % vol., gas pressure = 121.3 kPa and gas temperature = 298°K.

other is an intersection point between MEA and DEA curves representing the closeness in performance of CO<sub>2</sub> loading property at minimum gas velocity. Moreover, an increase in gas velocity and its effect on CO2 mass transfer rate highlights the simplicity of absorbent selection between MEA and DEA solutions. As discussed above, as the gas flow rate increases, the CO<sub>2</sub> flux declines steadily. In fact, the residence time of gas inside the shell is decreased by an increment of gas velocity. Then, lower amount of CO<sub>2</sub> is absorbed by the liquid phase even in the case that maximum concentration of the absorbent is used. With respect to liquid flow rate, Figure 10 shows the change in CO<sub>2</sub> flux versus to an increase in liquid velocity for MEA and DEA with equal concentration of 3 mol/litre. CO2 mass transfer through the membrane is highly dependent on the gradient of CO<sub>2</sub> concentration

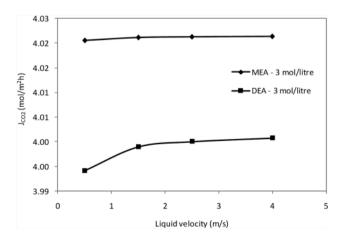


Figure 10: The effect of liquid velocity on  $CO_2$  mass transfer rate for different amines; Gas velocity = 5.5 m/s,  $CO_2$  concentration = 20 % vol., gas pressure = 121.3 kPa and gas temperature = 298°K.

on both sides. An increase in liquid velocity influences the  $CO_2$  concentration at the liquid interface and produces a higher concentration gradient. It causes improvement of the mass transfer coefficient, especially for DEA solutions. The rise of  $CO_2$  flux gradually continues, until the curve tends to level off after exceeding the effective flow rate. This can be attributed to the  $CO_2$  loading factor which is independent of liquid flow rate. As the absorbent velocity increases, the thickness of the mass boundary layer in the tube side decreases and improves the gas diffusion due to lower absorbent resistance. If the change in gas flow rate is considered to be negligible, the percentage of  $CO_2$  removal can be defined as follows:

$$\%CO_2 \, removal = 100 \, \frac{(Q \times C)_{inlet} - (Q \times C)_{outlet}}{(Q \times C)_{inlet}} \tag{21}$$

where Q and C denote the gas volumetric flow rate (m<sup>3</sup>/s) and mole concentration (mol/m<sup>3</sup>), respectively. The concentration of  $CO_2$  at the outlet of the shell side is calculated as follows:

$$C_{outlet} = \frac{\int C(r)dr}{\int dr}$$
 (22)

and the mass transfer rate of  $CO_2$  is expressed by the following equation:

$$J_{CO_2} = \frac{(Q \times C)_{inlet} - (Q \times C)_{outlet} \times 273.15 \times 1000}{22.4 \times T_g \times S}$$
(23)

where  $T_g$  (K) is the gas temperature and S (m<sup>2</sup>) is the total membrane area.

#### 6 Conclusions

The modelling of CO<sub>2</sub> absorption by different amine solutions in hollow fibre membrane was studied. A comprehensive mathematical model was presented to determine the CO<sub>2</sub> concentration at the product stream under various operating conditions. The model was developed based upon continuity equations including diffusion and convection in shell and tube sides, and axial and radial diffusions through the membrane. COMSOL software was used to numerically solve a system of non-linear partial differential equations using the finite element method. The result of the suggested model was compared with experimental data obtained from the literature and a good agreement was observed. An increase in gas flow rate decreased the CO<sub>2</sub> mass transfer rate due to reduction of residence time and increase in liquid flow rate resulted in better removal efficiency due to the change in mass transfer coefficient and the thickness of the absorbent boundary layer. Moreover, the flux of CO<sub>2</sub> could be improved by increasing absorbent concentration in the tube side due to availability of absorbent reactants at the gas-liquid interface. From three types of amine solution, MEA showed better performance for CO2 removal as compared to the DEA and MDEA solutions. The results of modelling highlighted the importance and credibility of this model in order to determine more accurate CO<sub>2</sub> concentration using diverse types of absorbent in the HFMCs. The model developed has also more capabilities to be run with other type of absorbents for the membrane separation system in terms of absorbent selection.

# **Nomenclature**

- membrane surface area (m<sup>2</sup>) Α
- C concentration (mol/m3)
- D diffusivity coefficient (m<sup>2</sup>/s)
- molar flux (mol/m<sup>2</sup>s)
- Н Henry's constant
- P pressure (bars)
- Q flow rate  $(m^3/s)$
- R reaction rate (mol/m<sup>3</sup>s)
- $r_1$ inner tube radius (mm)
- outer tube radius (mm)  $r_2$
- inner shell radius (mm)  $r_3$
- gas temperature (°C)  $T_g$
- velocity (m/s)

#### **Greek symbols**

module volume fraction η CO2 removal efficiency

#### **Abbreviations**

HFMC hollow fibre membrane contactor

DEA Diethanolamine MFA Monoethanolamine MDEA n-methyldiethanolamine

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