

Available online at www.sciencedirect.com

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

IChemE



Physical and reactive absorption of CO₂ in capillaries: Mass transfer, modelling and produced chemical species

Daniel O. Morales^a, Alejandro Regalado-Méndez^b, César Pérez-Alonso^c, Reyna Natividad^{a,*}

^a Chem. Eng. Lab., Centro Conjunto de Investigación en Química Sustentable CCIQS UAEM-UNAM, Universidad Autónoma del Estado de México, Carretera Toluca-Atlacomulco, km 14.5, C.P. 50200 Toluca, Mexico

^b Investigation laboratories, Campus Puerto Angel, Universidad del Mar, Puerto Angel 70902, Oaxaca, Mexico

^c Faculty of Chemistry, Universidad Autónoma del Estado de México, El Cerrillo Piedras Blancas, San Cayetano, Toluca, Mexico

ARTICLE INFO

Article history:

Received 26 May 2023

Received in revised form 19 August 2023

Accepted 28 August 2023

Available online 31 August 2023

Keywords:

Capillary reactors

CO₂ reactive absorptionCO₂ transport correlationCO₂ mass transfer

Taylor flow

ABSTRACT

In a circular economy and sustainability context, CO₂ utilization is key. For photochemical or electrochemical transformations, CO₂ absorption in liquids has become crucial and even a limiting step. This work aimed to establish an average mass transport coefficient ($\bar{k}_L a$) characteristic of the CO₂ absorption in water and in alkaline solutions in capillary absorbers (2–4 mm) under Taylor flow and recirculation mode. A correlation among prevailing dimensionless numbers (Sh, Re, Ca and Sc) was also established. To achieve so, the absorption of CO₂ was conducted in both, water and NaOH solutions (0.5 mol/dm³), and its concentration was monitored by measuring total inorganic carbon and pH. The gas and liquid flowrates used for the tests were 1.66×10⁻⁴ L/s and 2.5×10⁻⁴ L/s, respectively. The effect of temperature was investigated in the range of 283 and 308 K. The highest $\bar{k}_L a$ was found to be 12×10⁻² and 2.1×10⁻² s⁻¹, for water and NaOH solutions, respectively. The modelling and simulation of the carbon species formation and production was also conducted and a determination coefficient (R²) of 0.99 was found.

© 2023 Institution of Chemical Engineers. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, the capture of CO₂ that comes from industries through processes like absorption, is an attractive approach to prevent the emission of this gas to Earth's atmosphere. When CO₂ is absorbed in water and a chemical reaction is simultaneously carried out through catalytic processes such as photoreduction (Hurtado et al., 2016; Asiri and Lichtfouse, 2019; Karamian and Sharifnia, 2016) or electro-reduction (Asiri and Lichtfouse, 2019; Ganesh, 2016; Zhang

et al., 2020), this gas can be transformed into different fuels or fuel precursors, such as methanol, ethanol, and formic acid. Using only pure water as the liquid phase is not convenient since only absorbs a low amount of CO₂, so it is advisable to modify the chemical composition of the liquid phase to improve its effectiveness. In this context, aqueous solutions of alkali metal hydroxides have shown better performance (Ganapathy et al., 2013) and are commonly prepared with NaOH. Another element that also has a significant influence on the efficiency and control in the absorption process is the design of the absorber and the hydrodynamics that prevails in it. Devices with microscale technologies (composed of capillaries) have received great attention in recent years (Ganapathy et al., 2013; van Baten

* Corresponding author.

E-mail address: rnatividadr@uaemex.mx (R. Natividad).

<https://doi.org/10.1016/j.cherd.2023.08.045>

0263-8762/© 2023 Institution of Chemical Engineers. Published by Elsevier Ltd. All rights reserved.

Nomenclature

a	specific area (m^2/m^3)
A	interfacial area (m^2)
C	concentration (mol/m^3)
D	diameter (m)
$\mathcal{D}$	Diffusivity (m^2/s)
I	Ionic strength (mol/m^3)
k_L	Liquid-side mass transfer coefficient (m/s)
$\bar{k}_L$	Average liquid-side mass transfer coefficient (m/s)
$k_L a$	Liquid-side volumetric mass transfer coefficient (s^{-1})
$\bar{k}_L a$	Average liquid-side volumetric mass transfer coefficient (s^{-1})
$K_{L,diff}$	Overall liquid-side mass transfer coefficient by diffusion model (m/s)
$k_{1,1}$	Rate constant of first forward reaction ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
$k_{1,2}$	Rate constant of first backward reaction (s^{-1})
$k_{2,1}$	Rate constant of second forward reaction ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
$k_{2,2}$	Rate constant of second backward reaction (s^{-1})
$k_{3,1}$	Rate constant of third forward reaction (s^{-1})
$k_{3,2}$	Rate constant of third backward reaction ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
K_2	Equilibrium constant of second reaction (m^3/mol)
K_3	Equilibrium constant of third reaction (mol/m^3)
K_w	Water dissociation constant (mol^2/m^6)
$K_{A,1}$	First carbonic acid dissociation constant (mol/m^3)
$K_{A,2}$	Second carbonic acid dissociation constant (mol/m^3)
L	Length (m)
L_z	Penetration depth (m)
M	Molar mass (mol)
N	Number (Amount)
Q	Flow rate (mL/min)
r	Reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$)
t	time (s)
T	Temperature (K)
U	Velocity (m/s)

V	Volume (m^3)
W	Molar flux, absorption rate ($\text{mol m}^{-2} \text{s}^{-1}$)
z	Perpendicular direction to gas-liquid interface (m)

Greek letters

α	A_T/V_L (m^2/m^3)
δ	Film thickness (m)
μ	Viscosity (Pa·s)
ν	Valency
ρ	Density (kg/m^3)
σ	Surface tension (N/m)

Dimensionless numbers

Ca	Capillary number ($\mu_L \cdot U_{TP}/\sigma$)
E	Enhancement factor
Ha	Hatta number ($\sqrt{k_{1,1} \cdot \mathcal{D}_{CO_2} \cdot C_{OH^-}}/\bar{k}_L$)
$P(t)$	Time polynomial function
Re	Reynolds number ($U_{TP} \cdot D_{cap} \cdot \rho/\mu$)
Sc	Schmidt number ($\mu/\rho \cdot \mathcal{D}$)
Sh	Sherwood number ($k_L \cdot D_{cap}/\mathcal{D}$)
x	Molar fraction.

Subscripts

O	Initial
B	bubble
cap	Capillary
e	Equilibrium
F	Film
G	Gas
h	Hydraulic
i	Interface
j	Species
L	Liquid
S	Slug
Sob	Sobieszuk et al (Sobieszuk et al., 2011). method
sys	System
T	Total
TIC	Total Inorganic Carbon
$B1$	Mass balance in the entire unit cell
$B2$	Mass balance in the liquid film and slugs
w	water

Superscript

∞	infinite
----------	----------

and Krishna, 2004; Shao et al., 2010; Zhang et al., 2011; Sobieszuk et al., 2011; Zhu et al., 2017; Sattari-Najafabadi et al., 2018; Zhu et al., 2020). CO_2 absorption in capillaries is carried out under laminar flow and surface tension forces are dominant (Ganapathy et al., 2013; Akbar et al., 2003; Chen et al., 2006). Consequently, two-phase flow patterns, that can increase or decrease the gas-liquid interfacial area, are formed, e.g. slug flow, bubbly flow, and annular flow (Yue et al., 2007), depending on the relative gas and liquid velocities. Slug flow (or Taylor flow) is especially interesting because it is formed at low velocities of both phases and the gas-liquid interfacial area is relatively large (Ganapathy et al., 2013; Shao et al., 2010; Zhang et al., 2011; Sobieszuk et al., 2011; Kreutzer, 2003). The total volume of gas and liquid can be divided into unit cells that repeat throughout the capillary. Each unit cell is constituted by a liquid slug, a gas bubble, and a liquid film located between the gas bubble

and the channel wall. In the absorption of CO_2 in capillaries, the variation of the interfacial area between each bubble and the liquid phase along the channel plays an important role, since when a gas bubble encounters the liquid phase and flows through the channel, CO_2 dissolves and reacts (when there is another chemical specie like an alkali) (Zhu et al., 2017; Tan et al., 2012a, 2012b). In order to have a better understanding of the CO_2 absorption process without and with chemical reaction in capillaries with diameters in the range of 2–4 mm, it is essential to understand the hydrodynamic aspects that govern the behavior of these devices and, consequently, how they affect the rate of mass transfer. Therefore, the main objective of this work was to analyze the process of CO_2 absorption with and without chemical reaction in capillaries using aqueous NaOH solutions and water. For this, the work was divided into the following objectives:

- I. To establish the mass transfer coefficient for physical absorption of CO₂ in water, conducted in capillaries: comparison of two approaches.
- II. To elucidate the effect of hydrodynamics, temperature, and interfacial area on CO₂ physical and reactive absorption under Taylor flow with liquid-phase recirculation in capillaries with diameters of 2, 3 and 4 mm.
- III. To establish a mathematical model to predict the concentration profiles of the chemical species produced by the reactive absorption of CO₂ in alkaline solutions.
- IV. To establish correlations between dimensionless numbers that mathematically represent the mass transfer of CO₂ in physical and reactive absorption.

In addition, the results of this work aim to provide a guidance to establish operating conditions to conduct the transformation of CO₂ into carbonates and bicarbonates in capillaries, that can later be converted into other added value compounds via different paths like photocatalytic (Hurtado et al., 2016; Asiri and Lichtfouse, 2019; Karamian and Sharifnia, 2016; Adamu et al., 2023) or electrochemical (Asiri and Lichtfouse, 2019; Ganesh, 2016; Zhang et al., 2020; Bagemihl et al., 2022; Chang et al., 2023) processes. In this sense, it is important to mention that a process conducted in a capillary reactor is not scaled-up but scaled-out by adding further capillaries since once the behavior in one capillary is understood the others are to behave the same and this will mainly depend on the two-phase distribution achieved at the entrance of the capillaries bunch (Natividad et al., 2007). For this, co-current downflow contactors have been successfully assessed albeit in hydrogenation reactions (Natividad et al., 2004). In the context of CO₂ utilization, monoliths (structures constituted by thousands of capillaries) coated with a photocatalyst have been used to conduct the CO₂ transformation into valuable chemicals by photo-reduction in gas-phase (Tahir, 2018; Tahir and Amin, 2016).

2. Experiments and modelling

2.1. Absorption system

Fig. 1 shows the experimental set-up used for the CO₂ absorption. Gas and liquid phases were fed at the top of the capillary through a T-junction. They flowed within the capillary until being discharged in a container where the liquid phase was recirculated by a peristaltic pump (Masterflex, model 7557-12). The container shown in Fig. 1 was partially open to atmosphere so the non-absorbed CO₂ (depicted by the round bubbles in the solution in the container) could exit the system and in this way, pressurization was avoided. Temperature was kept constant according to the levels established in Table 1 by a thermal bath (not included in Fig. 1).

The experiments were performed with single glass capillaries of 30 cm length and circular cross-section of different inner diameters (2, 3 and 4 mm). A face-centered response surface design composed by 2^k factorial points, 2k axial points and 2k+1 center points was used to analyze the CO₂ absorption with and without chemical reaction at different temperatures and capillary diameters, so k=2. The lower, middle, and upper levels of the two different factors are reported in Table 1. The gas phase used for this research was composed mainly by CO₂ (mass fraction ≥99%, Grupo Infra S.A. de C.V., Mexico). A plausible application of this system is

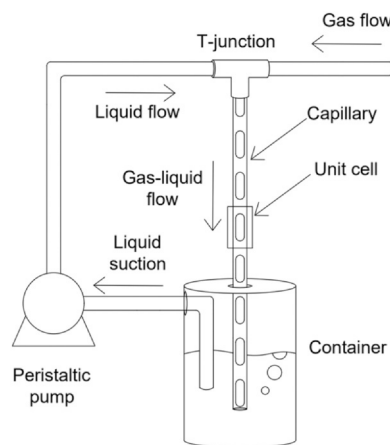


Fig. 1 – Experimental set-up for CO₂ absorption in a capillary channel.

Table 1 – Lower, middle, and upper levels of capillary diameter and temperature.

C _{NaOH,0} (M)	Factor	Level		
		-1	0	+1
0	D _{cap} (mm)	2	3	4
	T (K)	283	295.5	308
0.5	D _{cap} (mm)	2	3	4
	T (K)	283	295.5	308

the transformation of CO₂ into valuable chemicals and therefore the purity of the gas is important.

Two liquids, a 0.5 mol/dm³ NaOH aqueous solution and deionized water, were employed for the tests with and without chemical reaction, respectively; 60 mL were used for each run. Gas flow rate was 10 mL/min and liquid flow rate was 15 mL/min in each experiment, so the total flow rate of 25 mL/min results in a two-phase velocity inside the capillary, U_{TP}, that changes with diameter. Their values are listed in Table 2.

Film thickness was determined according to Eq. (1), considering that pressure drop is negligible due to laminar flow according to Reynolds numbers in Table S3 and Table 4 (Ganapathy et al., 2013; Shao et al., 2010; Aussillous and Quéré, 2000),

$$\delta = \frac{0.66Ca^{2/3}}{1 + 3.33Ca^{2/3}}D_{cap} \quad (1)$$

Specific areas of the capillary (a), liquid-slug surface (a_s) and film (a_f), were estimated from photographs taken with a Canon EOS Rebel SL3 camera equipped with a 55–250 mm telephoto lens, considering cylindrical-shape bubbles. This method is based on the conclusions reached by Sobieszuk et al (Sobieszuk et al., 2011), who obtained values relatively

Table 2 – Gas and liquid flow rate (Q_G and Q_L), and two-phase velocities (U_{TP}), used in the experiments with and without chemical reaction.

Q _L (mL/min)	Q _G (mL/min)	D _{cap} (mm)	U _{TP} × 10 ² (m/s)
15	10	2	13.26
		3	5.89
		4	3.32

close to those estimated by Danckwerts model (Danckwerts, 1970). However, they considered a semi-spherical geometry at the gas-liquid interface between the bubbles and slugs, so it is expected that the values calculated in this work be slightly different. The applied equations have been summarized in Section 1S of the supplementary material.

2.2. Mass transfer without chemical reaction

2.2.1. CO₂ concentration

The amount of CO₂ absorbed by the liquid phase was determined in each experiment as Total Inorganic Carbon concentration (C_{TIC}) since all the carbon involved in the system comes from the CO₂ dissolved in water. The equipment used for this analysis was a Total Organic Carbon Analyzer (Shimadzu Corporation, model TOC-L-_{CSN}), that also measures C_{TIC} .

2.2.2. Mass transfer in the entire system

Two approaches were used to calculate $k_L a$. In the first one (A1), a general balance was conducted based on the total system volume, V_{sys} , unlike other works where the base is V_{cap} . Here, mass transfer not only takes place inside the capillary, but the liquid volume in the container also participates in the CO₂ absorption. This part of liquid is not in direct and continuous contact with gas phase, but it modifies the process because the liquid volume within each unit cell mixes with it when leaves the capillary. For this reason, and for other phenomenological factors such as gas-liquid velocities, mass transfer occurs by convection and diffusion. C_{CO_2} in the liquid bulk in unit cell is theoretically similar as that in the container if CO₂ does not penetrate sufficiently during the time each unit cell stays inside the capillary. This means that ΔC_{CO_2} can be measured from the container. It was more convenient to study mass transfer focusing in V_L instead of V_{cap} for the correct estimation of k_L , and consequently, $k_L a$, which was calculated by means of solving Eq. (2),

$$\frac{dC_{CO_2}}{dt} = \bar{k}_L \alpha (C_{CO_2,i} - C_{CO_2}) \quad (2)$$

and taking into account that,

$$\bar{k}_L a = \bar{k}_L \alpha \frac{V_L}{V_{cap}} \quad (3)$$

The results obtained with this approach (A1) are shown in Table S2.

In the second approach (A2), CO₂ concentration over time and $\bar{k}_L a$ were estimated from another point of view in order to contrast the results obtained with A1. A2 approach considers that the film and the superficial zone of liquid slugs are the ones contributing the most to mass transfer resistance throughout the system compared to the inside of liquid slugs, where the absorbed CO₂ is perfectly mixed by the internal circulation after surpassing a penetration zone (Ganapathy et al., 2013) and therefore k_L changes throughout the process according to Higbie's penetration theory, so it is convenient to calculate an average value until reaching the equilibrium time (t_e),

$$\bar{k}_L = \frac{L_z}{t_e} \sum_{n=0}^{\infty} \frac{2(-1)^{2n}}{\left(n + \frac{1}{2}\right)^2 \pi^2} \left[1 - \exp\left(-\frac{\left(n + \frac{1}{2}\right)^2 \pi^2 \mathcal{D}_{CO_2}}{L_z^2} t_e\right) \right] \quad (4)$$

More details about the procedure to obtain Eq. (4) are given as supplementary material.

The values of $\bar{k}_L a$ from the surface of liquid slugs ($\bar{k}_L a_S$) and film ($\bar{k}_L a_F$) were calculated combining Eqs. (5S), (6S) and (4). Subsequently, the overall volumetric mass transfer coefficients were determined as follows (van Baten and Krishna, 2004; Sobieszuk et al., 2011; Tan et al., 2012b; Vandu et al., 2005) and they were compared to those obtained from A1 in order to establish their reliability.

$$\bar{k}_L a = \bar{k}_L a_S + \bar{k}_L a_F \quad (5)$$

2.3. Mass transfer with chemical reaction in a NaOH solution

2.3.1. Total CO₂ absorbed by liquid phase: experimental determination by pH and C_{TIC} measurements

CO₂ absorption in alkaline aqueous solutions produces HCO₃⁻ and CO₃²⁻ ions by means of the following reactions,



thus the C_{TIC} value that was determined by the analysis described in section 2.2.1 in the TOC analyzer, does not correspond only to C_{CO_2} in the liquid phase but it also includes the produced species, $C_{HCO_3^-}$ and $C_{CO_3^{2-}}$, originating Eq. (9),

$$C_{TIC} = C_{CO_2} + C_{HCO_3^-} + C_{CO_3^{2-}} \quad (9)$$

Each carbon species concentration in Eq. (9), was estimated by multiplying the results of Eqs. (10)–(12) by the value of C_{TIC} experimentally measured.

$$x_{CO_2} = \frac{1}{1 + \left(\frac{K_{A,1}}{C_{H^+}}\right) + \left(\frac{K_{A,1}K_{A,2}}{C_{H^+}^2}\right)} \quad (10)$$

$$x_{HCO_3^-} = x_{CO_2} \left(\frac{K_{A,1}}{C_{H^+}}\right) \quad (11)$$

$$x_{CO_3^{2-}} = x_{CO_2} \left(\frac{K_{A,1}K_{A,2}}{C_{H^+}^2}\right) \quad (12)$$

To determine C_{TIC} and C_{H^+} , samples were taken over 4 h and analyzed in the TOC analyzer and also with a pH meter. $K_{A,1}$ and $K_{A,2}$ are already reported in the literature as a function of T (Ganesh, 2016).

2.3.2. Modelling

The complexity of estimating C_{CO_2} in an absorption process with chemical reaction by means of the method described in section 2.2.2 increases because CO₂ is gradually consumed until the system reaches equilibrium. In this case, until the hydroxide ions be totally consumed. CO₂ is the only inorganic species that is transferred from gas phase to liquid phase, so all the inorganic carbon comes from there. Based on this, it can be affirmed that W_{CO_2} from the gas phase to liquid phase is equivalent to W_{TIC} , which depends on C_{TIC} without specifically involving the carbon species in the liquid phase. The influence of reaction on the absorption process is introduced by means of the enhancement factor, whose value is equal to 1 in

processes without reaction. Eq. (14) represents these considerations and is similar to Eq. (2),

$$W_{CO_2} \equiv W_{TIC} \quad (13)$$

$$\frac{dC_{TIC}}{dt} = Ek_L \alpha (C_{TIC,e} - C_{TIC}) \quad (14)$$

Nonetheless, E and k_L depend on time (Eq. (15)) according to Higbie's penetration theory (Krauß and Rzehak, 2017; Vas Bhat et al., 2000), while α changes due to the bubble size reduction within the capillary (Zhu et al., 2017; Tan et al., 2012a, 2012b). This fact becomes less evident as the system is closer to equilibrium. The inherent complexity of Eq. (14) solution, can be reduced by developing a polynomial function for $Ek_L \alpha$ from the experimental data, so Eq. (16) is obtained,

$$Ek_L \alpha \rightarrow P'(t) \quad (15)$$

$$\ln \left[\frac{C_{TIC,e}}{C_{TIC,e} - C_{TIC}} \right] = P(t) \quad (16)$$

Eq. (16) was used with experimental data to obtain $P(t)$. The C_{TIC} profile in the liquid phase was established with its exponential form,

$$C_{TIC} = C_{TIC,e} [1 - \exp(P(t))] \quad (17)$$

CO_2 absorption in alkaline aqueous solutions involves a complex reaction system in which CO_2 molecules interact with OH^- ions and water molecules, producing HCO_3^- and CO_3^{2-} ions as shown in Eqs. (6)–(8) (Krauß and Rzehak, 2017). The global rates of these reactions can be written as,

$$r_1 = k_{1,1} C_{CO_2} C_{OH^-} - k_{1,2} C_{HCO_3^-} \quad (18)$$

$$r_2 = k_{2,1} C_{OH^-} C_{HCO_3^-} - k_{2,2} C_{CO_3^{2-}} \quad (19)$$

$$r_3 = k_{3,1} C_{CO_2} - k_{3,2} C_{HCO_3^-} C_{H^+} \quad (20)$$

where C_{CO_2} , C_{OH^-} and C_{H^+} , can be found by Eqs. (9), (21) and (22),

$$C_{OH^-} = C_{OH^-,0} - C_{HCO_3^-} - 2C_{CO_3^{2-}} \quad (21)$$

$$C_{H^+} = \frac{K_w}{C_{OH^-}} \quad (22)$$

The reaction rate constant $k_{1,1}$ has already been given by Pohorecki and Moniuk (Pohorecki and Moniuk, 1988) as,

$$k_{1,1} = k_{1,1}^\infty \cdot 10^{\wedge} (0.221I - 0.016I^2) \quad (23)$$

where

$$k_{1,1}^\infty = 10^{\wedge} \left(-\frac{2382}{T} + 8.90 \right) \quad (24)$$

$$I = 0.5 \sum_j C_j v_j^2 \quad (25)$$

Reaction (6) is coupled with reaction (8) and water dissociation, so $k_{1,2}$ can be determined as suggested by Krauß and Rzehak (Krauß and Rzehak, 2017),

$$k_{1,2} = \frac{K_w}{K_3} k_{1,1} \quad (26)$$

As K_w changes with temperature, Tsonopoulos et al (Tsonopoulos et al., 1976). proposed an equation which describes its dependence on it. K_3 of reaction (8) can be estimated with the equation proposed by Edwards et al (Edwards et al., 1978),

$$K_w = \frac{(\rho_{H_2O})^2}{T^{22.48}} \cdot 10^{\wedge} \left[-\frac{5840}{T} + 61.21 \right] \quad (27)$$

$$K_3 = \frac{\rho_{H_2O}}{T^{36.78}} \cdot \exp \left[-\frac{12090}{T} + 235.5 \right] \quad (28)$$

The rate constant $k_{2,1}$ reaches very high values, so it is an instantaneous reaction. Even using $k_{2,1} = 10 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for all experiments does not have a significant influence in the results according to Krauß and Rzehak (Krauß and Rzehak, 2017). Then, $k_{2,2}$ can be calculated from $k_{2,1}$ as follows,

$$k_{2,2} = \frac{k_{2,1}}{K_2} \quad (29)$$

Hikita et al (Tsonopoulos et al., 1976). suggested Eq. (30) to determine K_2 , which has a dependence on C_{Na^+} and T ,

$$K_2 = K_2^\infty \cdot 10^{\wedge} \left(\frac{1.01 \sqrt{\frac{C_{Na^+}}{1000}}}{1 + 1.27 \sqrt{\frac{C_{Na^+}}{1000}}} + 0.125 \frac{C_{Na^+}}{1000} \right) \quad (30)$$

$$K_2^\infty = 10^{\wedge} \left(\frac{1567}{T} - 2.5866 - 0.006737^* T \right) \quad (31)$$

Reaction (8) does not involve ions, so the rate constants of the forward and backward reactions only depend on T as Johnson (Johnson, 1982) established,

$$k_{3,1} = \frac{1}{T^{183}} \cdot \exp \left[-\frac{61900}{T} + 1247 \right] \quad (32)$$

$$k_{3,2} = \frac{k_{3,1}}{K_3} \quad (33)$$

Finally, the general mass balances of each species in the liquid phase (MB) were established in a similar fashion as reported by Krauß and Rzehak (Krauß and Rzehak, 2017),

$$\frac{dC_{CO_2}}{dt} = -r_1 - r_3 \quad (34)$$

$$\frac{dC_{OH^-}}{dt} = -r_1 - r_2 \quad (35)$$

$$\frac{dC_{HCO_3^-}}{dt} = r_1 - r_2 + r_3 \quad (36)$$

$$\frac{dC_{CO_3^{2-}}}{dt} = r_2 \quad (37)$$

$$\frac{dC_{H^+}}{dt} = r_3 \quad (38)$$

Each species concentration in liquid phase was determined by simultaneous solution of Eqs. (17)–(38). The results of this model were compared with the data obtained with the method described in section 2.3.1.

3. Results and discussion

3.1. CO_2 absorption without chemical reaction

3.1.1. CO_2 concentration

An advantage of recirculating the liquid phase in the absorption process in capillaries is the increase of CO_2 concentration compared to systems without recirculation. Its behavior over time in systems without chemical reaction was described adequately by the methods A1 and A2 discussed in section 2.2.2, as shown in Fig. S1. A1 was focused on the general behavior of the concentration gradient in the

entire system, but A2 provided more information about the zones inside the capillary where CO₂ was being absorbed. The solution of Eq. (14S) for the film shows that it was instantly saturated and the solution for the superficial zone of each liquid slug provided a CO₂ concentration profile which depends on time and position as shown in Fig. S2. Eq. (14S) is a convergent solution of Eq. (11S) and only the first 50 terms of the infinite series were the most significant for this case, so $n = 50$. Each curve in Fig. S2 represents an approximation of CO₂ concentration throughout its penetration depth in the slug until it reaches the liquid bulk ($z = 0$), where the main mechanism of mass transfer changes from diffusion to convection. CO₂ penetration depth in liquid slugs during the unit-cell residence time became shorter mainly when temperature increased. The values are listed in Table S2.

The equilibrium of the absorption process in water was reached when CO₂ concentration at liquid bulk became the same as CO₂ concentration at gas-liquid interface, so

$$C_{CO_2,e} = C_{CO_2,i} \quad (39)$$

Equilibrium CO₂ concentration was expected to decrease when temperature increased because its desorption rate was higher, however, it also decreased slightly when the capillary diameter decreased as shown in Fig. S1 and Table S2. Furthermore, equilibrium CO₂ concentrations obtained in this work were lower than those estimated with Henry's Law. This is interesting because the literature specifies that saturation concentration only depends on system pressure and temperature. The experiments performed under the same conditions of these two factors should reach similar values of $C_{CO_2,i}$. However, the opposite is observed in Fig. S1 and Table S2. It should be considered that Henry's law does not specify the hydrodynamics, or the time required for an absorption system, to reach the saturation CO₂ concentration, so it is possible that $C_{CO_2,i}$ turns out to be apparently lower than expected. It might be that $C_{CO_2,i}$ became lower when using narrower capillaries because higher two-phase velocities increase the internal circulation of liquid phase and CO₂ desorption rate. Besides, higher values of U_{TP} lead to short residence times. The effect of unit-cell residence time on CO₂ absorption rate was not significant during the first minutes of these experiments because the liquid phase was not saturated, and mass transfer resistance was not high (see Fig. S1). However, the concentration gradient between the gas-liquid interface and liquid bulk took longer time to decrease as the process approaches the equilibrium according to Fig. S2. Here, the residence time must be longer to lead the liquid phase in unit cell to absorb as much CO₂ as possible before leaving the capillary, otherwise it will be more difficult for C_{CO_2} to increase as the system approaches equilibrium since even the CO₂ penetration in liquid phase starts again every time a new gas bubble enters the capillary. Mass transfer on CO₂ absorption also becomes better when more interfacial area is available. Wider single capillaries had higher A_T according to Table S1 because there were more bubbles inside them with larger radius compared to the narrower ones under the same gas and liquid flow rates.

3.1.2. Mass transfer coefficient

Mass transfer coefficient of a CO₂ absorption process in capillaries improves when U_{TP} is enhanced since the internal circulation of liquid slugs perfectly mixes the dissolved CO₂ throughout them (Shao et al., 2010). U_{TP} is higher when narrower capillaries are used, so $\bar{k}_L$ was better in experiments

Table 3 – Mass transfer parameters of CO₂ reactive absorption. $Q_L = 15$ mL/min, $Q_G = 10$ mL/min, $P_G = 419$ kPa, $C_{NaOH,0} = 0.5$ mol/dm³.

D_{cap} (mm)	T (K)	t_e (min)	$C_{TIC,e}$ (mol/m ³)	$k_{L,e}\alpha$ $\times 10^4$ (s ⁻¹)	$\bar{k}_{L,e}\alpha$ $\times 10^2$ (s ⁻¹)	$k_{L,e} \times 10^5$ (m/s)
2	283	180	551	2.38	1.51	1.35
2	295.5	180	519	2.31	1.47	1.31
2	308	180	516	2.65	1.69	1.50
3	283	120	533	7.43	2.10	2.88
3	295.5	130	515	7.05	2.00	2.73
3	295.5	118	512	7.28	2.06	2.81
3	295.5	150	516	6.97	1.97	2.69
3	295.5	150	520	7.17	2.03	2.77
3	295.5	130	516	6.81	1.93	2.63
3	308	130	513	6.97	1.97	2.69
4	283	130	540	11.82	1.88	3.38
4	295.5	125	522	12.57	2.00	3.59
4	308	110	513	11.71	1.86	3.34

performed with $D_{cap} = 2$ mm (see Table S2). $\bar{k}_L\alpha$, was higher in the experiments carried out with the widest single capillary ($D_{cap} = 4$ mm) because it had the largest A_T compared to the narrower ones under the same gas and liquid flow rates (see Tables 3 and 4).

This can be verified by looking at the decrease in t_e as D_{cap} increased under the same temperature conditions. However, $\bar{k}_L\alpha$ depends on the liquid volume that was used in each experiment and does not clearly reflect the intrinsic properties of capillaries under certain gas and liquid flows compared to $\bar{k}_L\alpha$. $\bar{k}_L\alpha$ represents the absorption rate per liquid volume while $\bar{k}_L\alpha$ represents the absorption rate per capillary volume, which changes according to capillary diameter (see Table S1). Narrower single capillaries have lower V_{cap} , so the number of bubbles within them is less compared to wider single capillaries under the same Q_L and Q_G . The interfacial area was evidently lower in narrower single capillaries, but it may become larger in a set of capillaries with smaller diameters that have the same volume as a wider single capillary. For this reason, $\bar{k}_L\alpha$ was higher in the experiments without chemical reaction carried out with $D_{cap} = 2$ mm (see Table S2) and it means that physical CO₂ absorption under Taylor flow with liquid phase recirculation may become more efficient in a set of capillaries with smaller diameters that has the same volume than a wider single capillary.

Table 4 – Dimensionless numbers of CO₂ absorption with chemical reaction. $Q_L = 15$ mL/min, $Q_G = 10$ mL/min, $P_G = 419$ kPa, $C_{NaOH,0} = 0.5$ mol/dm³.

D_{cap} (mm)	T (K)	Re_L	Re_G	Sc_L	$Ca \times 10^4$	$k_{L,e} \times 10^5$ (m/s)
2	283	263	53	278	18.0	1.35
2	295.5	351	49	349	14.0	1.31
2	308	439	46	345	11.0	1.50
3	283	175	35	278	8.0	2.88
3	295.5	234	33	349	6.0	2.73
3	295.5	234	33	349	6.0	2.81
3	295.5	234	33	349	6.0	2.69
3	295.5	234	33	349	6.0	2.77
3	295.5	234	33	349	6.0	2.63
3	308	293	30	345	5.0	2.69
4	283	131	26	278	4.5	3.38
4	295.5	176	25	349	3.4	3.59
4	308	220	23	345	3.0	3.34

$\bar{k}_L a$ is the mass transfer parameter which is typically used to compare two systems with different capillary diameters. Its estimation by means of methods A1 and A2 described in section 2.2.2 gave results that are similar to each other according to Fig. S3 and Table S2, so they are reliable values. However, method A2 provides more information about mass transfer in the unit cell. The film and the superficial zone of liquid slugs were the ones contributing to the overall volumetric mass transfer coefficient according to Eq. (5). The superficial zone of liquid slugs' contribution to $\bar{k}_L a$ improved with D_{cap} because its specific area, a_s , was higher thanks to the increasing of bubble diameter (see Tables S1 and S2). This is in agreement with the conclusions reached by Shao et al (Shao et al., 2010). On the other hand, it is normally expected that the film does not contribute significantly to CO_2 absorption because it is instantly saturated according to the values of $t_{e,F}$ listed in Table S2, but liquid-phase recirculation constantly renewed it, allowing it to absorb more CO_2 until the entire system reaches the equilibrium. As CO_2 penetration depth in the film was evidently shorter than in liquid slugs according to Table S2, the mass transfer resistance was also reduced. Therefore, $\bar{k}_L a_F > \bar{k}_L a_S$. Based on the results reported in Table S2, it can be inferred that the unit cell element contributing the most to $\bar{k}_L a$ during CO_2 absorption in systems under Taylor flow with liquid-phase recirculation is the film. $\bar{k}_L a$ also increases slightly with temperature because the film becomes thinner with it (penetration depth, δ , is shorter). The experiments performed with higher temperatures showed the highest values of $\bar{k}_L a$, but equilibrium CO_2 concentration was lower according to Fig. S1 and Table S2.

All values related to bubble size in the chemical reaction scenario listed in Table S1 are reached values when bubble size reduction is no longer significant.

3.1.3. Hydrodynamics effect on CO_2 physical absorption

The overall effect of hydrodynamic parameters such as U_{TP} , D_{cap} , T , Q_L and Q_G , on CO_2 absorption without chemical reaction in capillaries was established through dimensionless numbers Re_L , Re_G and Ca . $\bar{k}_L a$ was enhanced when Re increases as shown in Table S3, although it should be considered that CO_2 desorption rate also increases with it. In general, mass transfer improves when gas and liquid phases are in motion, but the effect becomes less significant after a certain point (Shao et al., 2010). Capillary number describes the effect of U_{TP} , liquid viscosity, and surface tension on film thickness. Higher values of Ca result in thicker films. The increase in δ with Ca is a positive aspect because it means that there is more liquid available in the film to absorb CO_2 , and the time to reach equilibrium decreases since it contributes even more to mass transfer. Re_L , Re_G , and Ca , are correlated to each other because all of them depend on U_{TP} .

Since $\bar{k}_L a$ depends on all the hydrodynamic parameters above mentioned, a dimensionless correlation was established between the numbers Re_L , Re_G , Ca , Sh_L and Sc_L , to facilitate their estimation. A regression analysis on all the results listed in Table S3 led to the relationship,

$$Sh_L a D_{cap} = 5.96 \times 10^8 \quad Re_L^{1.41} Re_G^{-4.93} Sc_L^{1.17} Ca^{1.64} \quad (40)$$

The positive parameters of Re_L and Ca , show how faster two-phase flow improve Sherwood number and, consequently, the mass transfer coefficient in CO_2 absorption without chemical reaction. The negative parameter of Re_G could be attributed to the decrease in Taylor flow stability

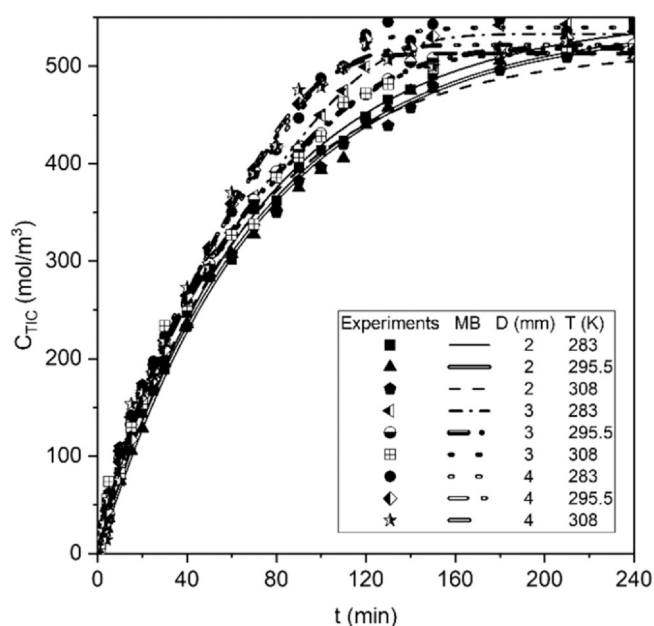


Fig. 2 – Comparison between C_{TIC} measured experimentally and predicted with Eq. (17). $Q_L = 15 \text{ mL/min}$, $Q_G = 10 \text{ mL/min}$, $P_G = 419 \text{ kPa}$, $C_{NaOH,0} = 0.5 \text{ mol/dm}^3$.

with the increase in gas-phase velocity. The values estimated with Eq. (40) were close to those determined experimentally by the method described in section 2.2.2 according to Fig. 3, so its implementation is valid for Re_L in the range 131–439, Re_G in the range 23–53, Sc_L in the range 278–349, and $Ca \times 10^4$ in the range 3–18. It is recommendable to use the same proportional relation between Q_L and Q_G of this work for the estimation of $\bar{k}_L a$ with the dimensionless correlation (40), since different combinations of Q_L and Q_G can produce two-phase flows with the same Re_L , Re_G , and Ca , but different interfacial areas and $\bar{k}_L a$.

3.2. CO_2 reactive absorption

3.2.1. Species concentration and pH

As mentioned in section 3.1.1, an advantage of recirculating the liquid phase in the absorption process in capillaries is the increase in the total amount of CO_2 absorbed compared to systems without recirculation. Its value is further enhanced when using NaOH aqueous solutions rather than pure water, although the interaction between CO_2 and OH^- ions produces a mixture of inorganic carbon species that complicates the monitoring of W_{CO_2} in liquid phase. W_{CO_2} is equivalent to W_{TIC} according to section 2.3.2, and this reduces the complexity of describing its overall behavior. Fig. 2 shows that D_{cap} modified the time when equilibrium was reached. Here, the experiments carried out with $D_{cap} = 4 \text{ mm}$ were the ones that showed the best performance. Wider capillaries had lower U_{TP} and longer residence times compared to narrower capillaries under the same Q_L and Q_G . The unit-cell residence time did not significantly influence the absorption rate during the first minutes of the process because the reaction rate between CO_2 and OH^- ions was high enough that all the CO_2 in each bubble was consumed completely before leaving the channel. This can be noted visually by bubble size reduction along the capillary as shown in Fig. 3. Take, for instance, the image at 25 min in Fig. 3, where the bubble size at the capillary entrance is 18.6 mm and is reduced to 7.4 mm almost

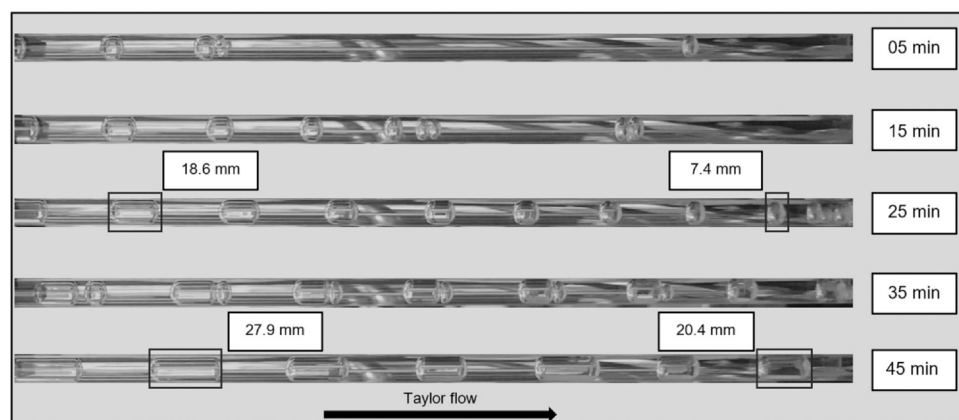


Fig. 3 – Effect of reaction time on bubble size along the capillary. $Q_L = 15 \text{ mL/min}$, $Q_G = 10 \text{ mL/min}$, $P_G = 419 \text{ kPa}$, $C_{\text{NaOH},0} = 0.5 \text{ mol/d m}^3$.

at the capillary exit because of the CO_2 consumption. However, the absorption and reaction rates dropped as time passed due to the OH^- ions depletion in the liquid phase, leading to a less evident bubble size reduction along the capillary at longer times. This is evident at 45 min in Fig. 3 where the bubble length was only reduced 7.5 mm. At this point, the unit-cell residence time exerts an important effect on CO_2 absorption.

The gradual change of the species concentration in the liquid phase due to their interaction described by reactions (6)–(8) provided more information about the behavior discussed previously. C_j was determined by measuring the pH according to the method described in section 2.3.1. Carbonate ions predominate when pH is high; bicarbonate ions at intermediate pH values; and CO_2 when pH reaches low values as shown in Fig. S5. pH followed the same path as C_{TIC} according to Fig. 4. It did not show significant changes when residence time was modified by the expansion or reduction of D_{cap} during the first minutes of each experiment,

but it decreased more quickly after a certain point. C_{TIC} and pH had this behavior because the excess concentration of OH^- ions at the beginning consumed all the dissolved CO_2 until being converted into CO_3^{2-} ions as shown in Fig. 5. The reaction rate was high enough that all the CO_2 was instantly consumed at the gas-liquid interface before the unit cell leaves the capillary (see Fig. 3), so $C_{\text{OH}^-} - y C_{\text{CO}_3^{2-}}$ did not present significant changes with D_{cap} and residence time variation during the first minutes of the process as shown in Fig. 6c and d. However, C_{OH^-} was quickly depleted as time goes by and backward reaction (7) and reaction (8) took on greater importance when its value was no longer significant. Then, $C_{\text{CO}_3^{2-}}$ started to decrease and $C_{\text{HCO}_3^-}$ to increase as shown in Fig. 5. From this point, the residence time contribution to CO_2 absorption rate became relevant because the CO_2 in each bubble was no longer consumed completely by the liquid phase of unit cell according to Fig. 3. Backward reaction (7) and reaction (8) were much slower than reaction (6) and

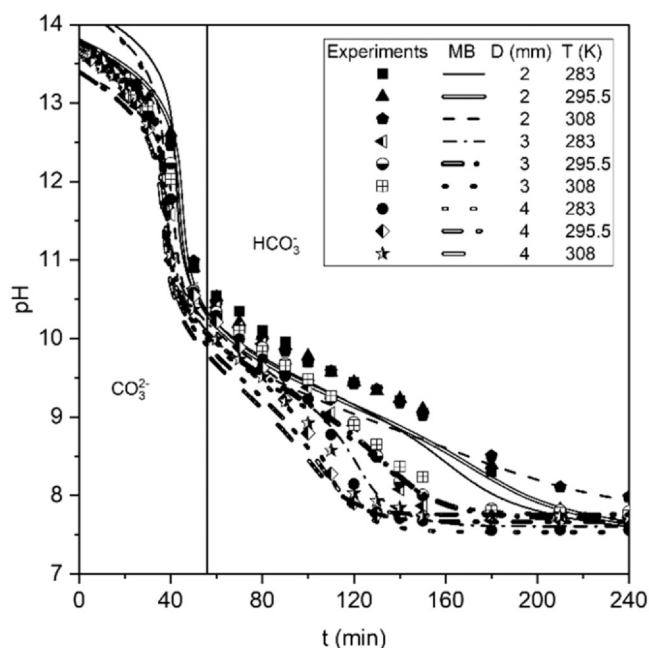


Fig. 4 – Comparison between pH measured experimentally and estimated combining Eqs. (17)–(38). $Q_L = 15 \text{ mL/min}$, $Q_G = 10 \text{ mL/min}$, $P_G = 419 \text{ kPa}$, $C_{\text{NaOH},0} = 0.5 \text{ mol/dm}^3$.

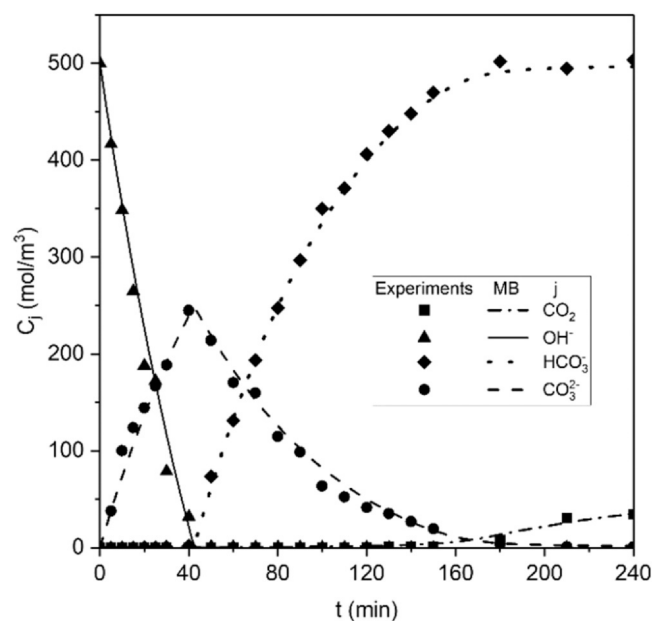


Fig. 5 – Species concentration determined experimentally and estimated combining Eqs. (17)–(38). $T = 283 \text{ K}$, $D_{\text{cap}} = 2 \text{ mm}$, $Q_L = 15 \text{ mL/min}$, $Q_G = 10 \text{ mL/min}$, $P_G = 419 \text{ kPa}$, $C_{\text{NaOH},0} = 0.5 \text{ mol/dm}^3$.

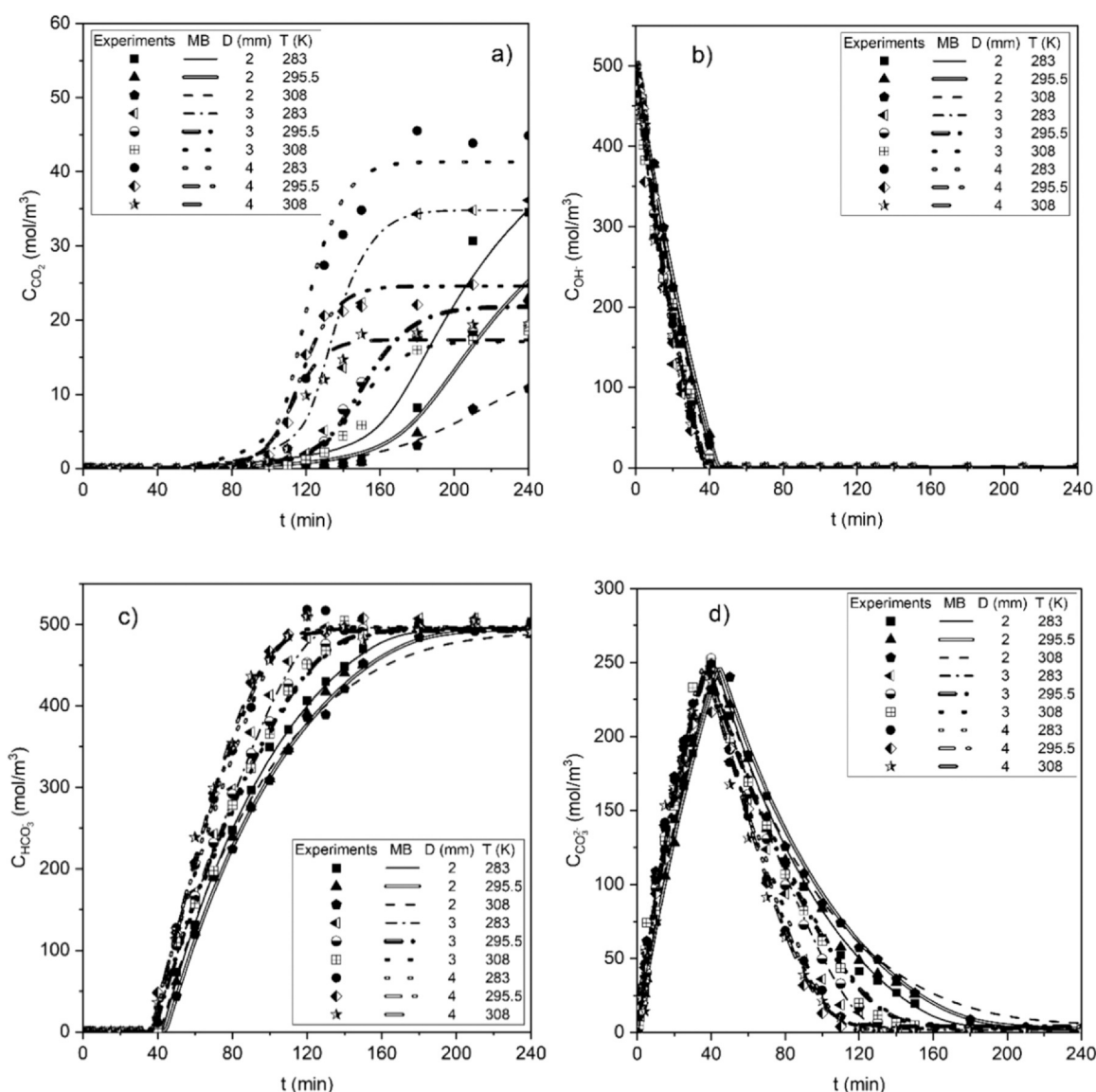


Fig. 6 – C_i determined experimentally and estimated combining Eqs. (17)–(38). $Q_L = 15$ mL/min, $Q_G = 10$ mL/min, $P_G = 419$ kPa, $C_{NaOH,0} = 0.5$ mol/dm³.

forward reaction (7), so CO_2 molecules had the opportunity to penetrate deeper into liquid phase. Residence time must be longer in order to lead the liquid phase in unit cell to capture as much CO_2 as possible before leaving the capillary. Wider capillaries were the ones providing longer residence times under the same conditions of Q_L and Q_G , so $C_{HCO_3^-}$ increased more quickly while $C_{CO_3^{2-}}$ decreased as shown in Fig. 6c and d. For this reason, C_{TIC} and pH also increased and decreased, respectively, in less time when $D_{cap} = 4$ mm. The reactions continued until equilibrium was reached, when all the CO_3^{2-} ions had been converted to HCO_3^- ions, but liquid phase still absorbed CO_2 physically until its concentration also reached the equilibrium according to Fig. 5. Another factor that improves the CO_2 absorption rate is the increasing of interfacial area. Wider single capillaries were the ones providing larger A_T under the same conditions of Q_L and Q_G according to Table S1.

Compared to D_{cap} , temperature did not have a significant effect on CO_2 absorption rate within the studied range in this work as shown in Fig. 2. The reaction rate between CO_2 and OH^- ions improves with temperature according to the

conclusions reached by Ganapathy et al (Ganapathy et al., 2013), but even at low temperatures this was still instantaneous, so CO_2 in each bubble was always consumed completely before leaving the capillary during the first minutes of the process under the same conditions of Q_L and Q_G . The influence of temperature should be more evident when C_{OH^-} is depleted since backward reaction (7) also improves with it. However, physical CO_2 absorption represented by reaction (8) follows the opposite path as discussed in section 3.1.1. In the end, their effect was offset to each other, and the temperature variation did not affect the CO_2 absorption rate.

The absence of molecular C_{CO_2} during most of the experiment, indicates that all the CO_2 captured by the reaction effect was converted completely into other inorganic species until the reactions reached the equilibrium according to Fig. 5. This means that the total amount of CO_2 that can be absorbed by the reaction effect is independent of capillary diameter and temperature. Therefore, the slight difference in the values of $C_{TIC,e}$ reported in Table 3 was mainly attributed to physical absorption, which depends evidently on these two factors as discussed in section 2.2.1 and shown in Fig. 6a.

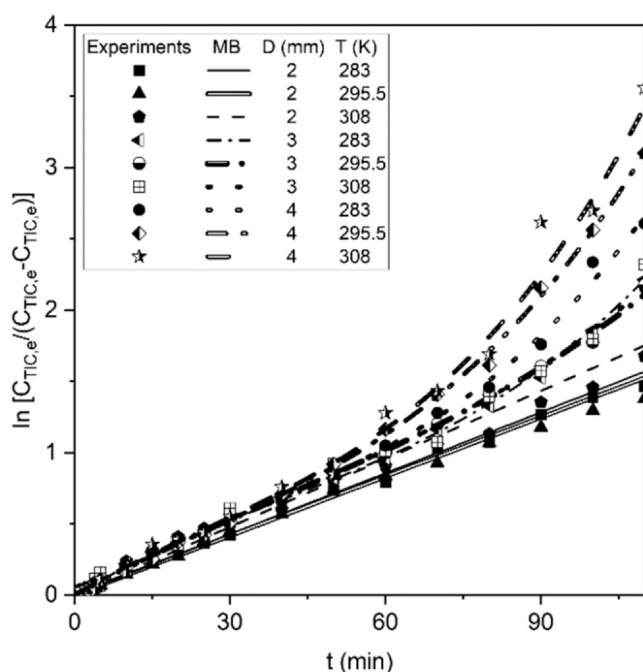


Fig. 7 – Behavior of $\ln [C_{TIC,e} / (C_{TIC,e} - C_{TIC})]$ as a function of time (Eq. (16)). $Q_L = 15 \text{ mL/min}$, $Q_G = 10 \text{ mL/min}$, $P_G = 419 \text{ kPa}$, $C_{NaOH,0} = 0.5 \text{ mol/dm}^3$.

3.2.2. Absorption rate

In section 2.3.1, a series of steps to predict the total inorganic carbon concentration, pH, and species concentration over time was described. The results are shown in Fig. 2, Fig. 4 and Fig. 6. Accordingly, CO_2 absorption rate depends mainly on three factors: the reaction rate, represented by the enhancement factor; the mass transfer coefficient; and the interfacial area. The overall effect of their combination in each experiment, $Ek_L\alpha$, is the slope of $P(t)$ shown in Fig. 7. The determination of the individual value of these factors is complex because they change over time until equilibrium is reached; thus, its influence on the CO_2 absorption rate was described more easily by comparing the results obtained under the different conditions. The reaction rate did not show significant changes within the temperature range used in this work as discussed in the previous section. Besides, the capillary diameter had no effect on it, so E values in each run must have been close to each other. E gradually decreases as the reactions approach the equilibrium (Krauß and Rzehak, 2017), so $Ek_L\alpha$ should follow the same path. However, it should be noted that bubble size reduction was less evident with time as shown in Fig. 3. This means that the interfacial area available inside the capillary constantly increased until it reached its maximum value reported in Table S1. The bubble size reduction occurred in the same proportion with $D_{cap} = 2\text{--}4 \text{ mm}$ under the same Q_L and Q_G because OH^- ions concentration was high enough to consume all the CO_2 contained in each bubble before the unit cell leaves the capillary. It can be inferred that $Ek_L\alpha$ hardly changed with temperature and capillary diameter during the first minutes of all experiments and remained relatively constant during the same period because the decrease in E was proportional to the increase in A_T (see Fig. 7). The effect of k_L was irrelevant during most of this time interval because CO_2 reacted instantly at the gas-liquid interface with OH^- ions and did not penetrate the liquid phase, so mass transfer resistance remained the same. Here, CO_2 absorption rate was contributed

mainly by reaction rate. This affirmation is reliable as long as $Ha \gg 1$ which is the case according to Fig. S7 during an important period of time. However, the whole situation changed when OH^- ions concentration was depleted. From this point, subsequent reactions became slower, so CO_2 was no longer consumed completely at the liquid-phase surface and began to penetrate it more frequently as its interaction with ionic species decreased. This means that it was possible for k_L to gradually increase until backward reaction (7) and reaction (8) finished. The experiments where these reactions generally reached equilibrium earlier were those performed with $D_{cap} = 4 \text{ mm}$ according to Table 3. Wider single capillaries were the ones providing longer residence times that allowed the liquid phase of each unit cell to capture more CO_2 before leaving the capillary. Consequently, the concentration of ionic species that can react with CO_2 decreased more quickly, allowing k_L to become higher. In addition, bubble size reduction was no longer significant, so A_T was noticeably larger in single capillaries with larger diameters under the same Q_L and Q_G . The decrease in E was no longer proportional to the increase in A_T , but A_T increased much more than E decreased. In the end, $Ek_L\alpha$ improved and became even better when D_{cap} increased according to Fig. 7.

CO_2 absorption rate in the second part of the process was contributed mainly by mass transfer, which also defined the time in which C_{TIC} reached the equilibrium. This affirmation is reliable as long as $Ha < 1$. Here, $k_L\alpha$ was more relevant than E , but both changed with time and there was no easy way to estimate their values separately before the reactions ended. $E = 1$ when that point was reached, so only $k_L\alpha$ remained. In Table 3, $k_{L,e}\alpha$ represents the influence of D_{cap} and unit-cell residence time on mass transfer rate during this period. $k_{L,e}\alpha$ improved with increasing these factors for the same reasons as $Ek_L\alpha$. These data are reliable because all the results obtained according to that described in section 2.3.1, fit adequately the experimental data according to Fig. 2, Fig. 4 and Fig. 6. However, $k_{L,e}\alpha$ only considers the interfacial area inside each single capillary in these experiments and does not reflect the intrinsic properties of capillaries under given gas and liquid flow rates compared to $k_{L,e}a$ that considers the interfacial area per capillary volume as already discussed in section 3.1.2. $k_{L,e}a$ was expected to increase when D_{cap} decreased such as the no-reaction scenario because the mass transfer area becomes larger in a set of capillaries with smaller diameters that represents the same volume of a capillary with wider diameter. The values reported in Table 3 indicate the opposite even though the variation is not significant, so CO_2 absorption rate in a capillary with wider diameter would still be better than in a set of capillaries with smaller diameters that represent the same volume during this period. This happens because $k_{L,e}$ and a follows opposite trends. Wider single capillaries have larger specific areas according to Table S1, but mass transfer coefficients are higher in wider capillaries as shown in Table 3 because the residence times of unit cell in them are longer. In the end, $k_{L,e}$ is the mass transfer parameter that best describes the CO_2 absorption rate and depends mainly on D_{cap} and unit-cell residence time as well as $Ek_L\alpha$ and $k_{L,e}\alpha$.

3.2.3. Hydrodynamics and CO_2 absorption in NaOH aqueous solutions

The period between the OH^- ions depletion and reaction equilibrium is the controlling step of CO_2 absorption process with chemical reaction in capillaries with liquid-phase

recirculation, so it is the main approach of $k_{L,e}$. The overall effect of hydrodynamic parameters such as U_{TP} , D_{cap} , T , Q_L and Q_G , on $k_{L,e}$ can be figured out through the dimensionless numbers Re_L , Re_G and Ca , but their value is mainly related to unit-cell residence time. Lower Re_L , Re_G and Ca under the same temperature conditions indicate higher unit-cell residence times, so $k_{L,e}$ is enhanced according to Table 4. Re_L , Re_G and Ca , are correlated to each other because all of them depend on U_{TP} .

It was decided to establish a dimensionless correlation between the numbers Re_L , Re_G , Ca , Sh_L and Sc_L , in order to facilitate the estimation of $k_{L,e}$. A regression analysis on all the results listed in Table 4 gave the relationship,

$$Sh_{L,e} = 4.1 \times 10^{-10} Re_L^{-0.29} Re_G^{1.68} Sc_L^{1.21} Ca^{-1.87} \quad (41)$$

The negative parameters of Re_L and Ca , show how $k_{L,e}$ is enhanced by using slower two-phase flows when OH^- ions have been depleted in CO_2 absorption with chemical reaction. The values estimated with Eq. (41) were close to those determined experimentally by the method described in section 2.3.1 according to Fig. 6, so its implementation is valid for Re_L in the range 131–439, Re_G in the range 23–53, Sc_L in the range 278–349, and $Ca \times 10^4$ in the range 3–18. It is recommendable to use the same proportional relation between Q_L and Q_G of this work for the estimation of $k_{L,e}$ with the dimensionless correlation (41), since different combinations of Q_L and Q_G can produce two-phase flows with the same Re_L , Re_G and Ca , but different interfacial areas and $k_{L,e}$.

It can be observed in Table 4 that the absorption rate is higher in wider single capillaries because they have larger interfacial areas and longer unit-cell residence times than narrower single capillaries under the same gas and liquid flow rates. However, it is necessary to have the same capillary volume in all the experiments in order to make the comparison between them fair. A set of capillaries with smaller diameters that have the same volume as a capillary with wider diameter may be more efficient in CO_2 absorption according to the values of $\bar{k}_L a$ obtained in this work, which are in the range $3\text{--}12 \times 10^{-2} \text{ s}^{-1}$. Mass transfer can be enhanced when increasing the two-phase velocity since the internal circulation of slugs mixes efficiently the absorbed CO_2 in liquid phase. The effect of unit-cell residence time and interfacial area on CO_2 absorption rate with chemical reaction is not significant during the first minutes of the process because the CO_2 contained in bubbles is instantly consumed by liquid phase thanks to the excess of OH^- ions. Here, CO_2 absorption rate is contributed mainly by reaction rate. Based on this, it is recommendable to increase the gas and liquid flow rates during this period to accelerate the total inorganic carbon accumulation as long as all the CO_2 which is fed is consumed completely before leaving the capillary. CO_2 no longer reacts instantaneously at gas-liquid interface when OH^- ions are depleted, so residence time and interfacial area become relevant as they must be as high as possible in order to lead the liquid phase of unit cell to absorb as much CO_2 as possible before leaving the capillary. CO_2 absorption rate is contributed mainly by mass transfer during this time interval which is the controlling step of the entire process. Wider single capillaries provide longer residence times, so they have better mass transfer coefficients. All the values of $k_{L,e}$ obtained in this work are in the range $1.31\text{--}3.59 \times 10^{-5} \text{ m/s}$. As in the no-reaction scenario, CO_2 absorption process with chemical reaction under Taylor flow with liquid-phase recirculation is expected to be better in a set of capillaries of

smaller diameters that have the same volume as a capillary with wider diameter because the interfacial area they provide is larger, but the results of this work indicate the opposite. The absence of CO_2 during most of the time each experiment lasted indicates that all the CO_2 captured by the reaction effect is converted completely into other inorganic species. Carbonate ions predominate as long as OH^- ions concentration is not depleted, then they are gradually transformed into bicarbonate ions until the system reaches equilibrium.

4. Conclusions

In this work, the effect of hydrodynamics, temperature, and interfacial area on CO_2 absorption with and without chemical reaction under Taylor flow with liquid-phase recirculation was studied in capillaries with diameters of 2, 3 and 4 mm. $\bar{k}_L a$ obtained in this work are in the range $3\text{--}12 \times 10^{-2} \text{ s}^{-1}$ when the absorption of CO_2 is only physical.

When the absorption of CO_2 is reactive, it is advised to increase the gas and liquid flow rates to accelerate the total inorganic carbon accumulation as long as all the fed CO_2 is consumed completely before leaving the capillary. Wider single capillaries provide longer residence times, so they have better mass transfer coefficients. All the values of $k_{L,e}$ obtained in this work are in the range $1.3\text{--}3.6 \times 10^{-5} \text{ m/s}$. Under this scenario, all the CO_2 captured by the reaction effect is converted completely into other inorganic species. Carbonate ions predominate as long as OH^- ions concentration is not depleted, then they are gradually transformed into bicarbonate ions until the system reaches equilibrium.

Two correlations between dimensionless numbers were obtained for the physical and reactive absorption, these being, respectively,

$$Sh_L a D_{cap} = 5.96 \times 10^8 Re_L^{1.41} Re_G^{-4.93} Sc_L^{1.17} Ca^{1.64}$$

$$Sh_{L,e} = 4.1 \times 10^{-10} Re_L^{-0.29} Re_G^{1.68} Sc_L^{1.21} Ca^{-1.87}$$

A mathematical model to predict the concentration profiles of the produced chemical species in the CO_2 reactive absorption was established and provides an excellent fitting of the experimental results.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Daniel Morales is grateful to CONACYT for providing financial support to complete postgraduate studies (Scholarship 776472). The financial support of Universidad Autónoma del Estado de México through project 6542/2022CI is also acknowledged. The technical support of Citlalit Martínez is greatly appreciated.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.cherd.2023.08.045](https://doi.org/10.1016/j.cherd.2023.08.045).

References

- Hurtado, L., Natividad, R., García, H., 2016. Photocatalytic activity of Cu₂O supported on multi layers graphene for CO₂ reduction by water under batch and continuous flow. *Catal. Commun.* 84, 30–35.
- Asiri, A.M., Lichtfouse, E., 2019. *Convers. Carbon Dioxide into Hydrocarb.* Vol. 1: Catal. ; Vol. 2: Technol.
- Karamian, E., Sharifnia, S., 2016. On the general mechanism of photocatalytic reduction of CO₂. *J. CO₂ Util.* 16, 194–203.
- Ganesh, I., 2016. Electrochemical conversion of carbon dioxide into renewable fuel chemicals - the role of nanomaterials and the commercialization. *Renew. Sustain. Energy Rev.* 59, 1269–1297.
- Zhang, F., Chen, C., Tang, Y., Cheng, Z., 2020. CO₂ reduction in a microchannel electrochemical reactor with gas-liquid segmented flow. *Chem. Eng. J.* 392, 124798.
- Ganapathy, H., Al-Hajri, E., Ohadi, M., 2013. Mass transfer characteristics of gas-liquid absorption during Taylor flow in mini/microchannel reactors. *Chem. Eng. Sci.* 101, 69–80.
- van Baten, J.M., Krishna, R., 2004. CFD simulations of mass transfer from Taylor bubbles rising in circular capillaries. *Chem. Eng. Sci.* 59, 2535–2545.
- Shao, N., Gavrilidis, A., Angeli, P., 2010. Mass transfer during Taylor flow in microchannels with and without chemical reaction. *Chem. Eng. J.* 160, 873–881.
- Zhang, T., Cao, B., Fan, Y., Gonthier, Y., Luo, L., Wang, S., 2011. Gas-liquid flow in circular microchannel. Part I: influence of liquid physical properties and channel diameter on flow patterns. *Chem. Eng. Sci.* 66, 5791–5803.
- Sobieszuk, P., Pohorecki, R., Cygański, P., Grzelka, J., 2011. Determination of the interfacial area and mass transfer coefficients in the Taylor gas-liquid flow in a microchannel. *Chem. Eng. Sci.* 66, 6048–6056.
- Zhu, C., Lu, Y., Fu, T., Ma, Y., Li, H.Z., 2017. Experimental investigation on gas-liquid mass transfer with fast chemical reaction in microchannel. *Int. J. Heat. Mass Transf.* 114, 83–89.
- Sattari-Najafabadi, M., Nasr Esfahany, M., Wu, Z., Sundén, B., 2018. Mass transfer between phases in microchannels: a review. *Chem. Eng. Process. - Process. Intensif.* 127, 213–237.
- Zhu, K., Yao, C., Liu, Y., Chen, G., 2020. Theoretical approach to CO₂ absorption in microreactors and reactor volume prediction. *Chem. Eng. Process. - Process. Intensif.* 150, 107904.
- Akbar, M.K., Plummer, D.A., Ghiaasiaan, S.M., 2003. On gas-liquid two-phase flow regimes in microchannels. *Int. J. Multiph. Flow.* 29, 855–865.
- Chen, L., Tian, Y.S., Karayiannis, T.G., 2006. The effect of tube diameter on vertical two-phase flow regimes in small tubes. *Int. J. Heat. Mass Transf.* 49, 4220–4230.
- Yue, J., Chen, G., Yuan, Q., Luo, L., Gonthier, Y., 2007. Hydrodynamics and mass transfer characteristics in gas-liquid flow through a rectangular microchannel. *Chem. Eng. Sci.* 62, 2096–2108.
- Kreutzer, M.T., 2003. *Hydrodyn. taylor Flow. capillaries Monolith React.*
- Tan, J., Lu, Y.C., Xu, J.H., Luo, G.S., 2012a. Mass transfer characteristic in the formation stage of gas-liquid segmented flow in microchannel. *Chem. Eng. J.* 185–186, 314–320.
- Tan, J., Lu, Y.C., Xu, J.H., Luo, G.S., 2012b. Mass transfer performance of gas-liquid segmented flow in microchannels. *Chem. Eng. J.* 181–182, 229–235.
- Adamu, A., Isaacs, M., Boodhoo, K., Russo Abegao, F., 2023. Investigation of Cu/TiO₂ synthesis methods and conditions for CO₂ photocatalytic reduction via conversion of bicarbonate/carbonate to formate. *J. CO₂ Util.* 70, 1–16.
- Bagemihl, I., Bhatraju, C., van Ommen, J.R., van Steijn, V., 2022. Electrochemical reduction of CO₂ in tubular flow cells under gas-liquid taylor flow. *ACS Sustain. Chem. Eng.* 10, 12580–12587.
- Chang, B., Pang, H., Raziq, F., Wang, S., Huang, K., Ye, J., Zhang, H., 2023. Electrochemical reduction of carbon dioxide to multicarbon (C₂+) products: challenges and perspectives. *Energy Environ. Sci.* <https://doi.org/10.1039/d3ee00964e>
- Natividad, R., Cruz-Olivares, J., Fishwick, R.P., Wood, J., Winterbottom, J.M., 2007. Scaling-out selective hydrogenation reactions: From single capillary reactor to monolith. *Fuel* 86, 1304–1312.
- Natividad, R., Kulkarni, R., Nuithitikul, K., Raymahasay, S., Wood, J., Winterbottom, J.M., 2004. Analysis of the performance of single capillary and multiple capillary (monolith) reactors for the multiphase Pd-catalyzed hydrogenation of 2-butyne-1,4-diol. *Chem. Eng. Sci.* 5431–5438.
- Tahir, M., 2018. Photocatalytic carbon dioxide reduction to fuels in continuous flow monolith photoreactor using montmorillonite dispersed Fe/TiO₂ nanocatalyst. *J. Clean. Prod.* 170, 242–250.
- Tahir, M., Amin, N.A.S., 2016. Performance analysis of nanostructured NiO-In₂O₃/TiO₂ catalyst for CO₂ photoreduction with H₂ in a monolith photoreactor. *Chem. Eng. J.* 285, 635–649.
- Aussillous, P., Quéré, D., 2000. Quick deposition of a fluid on the wall of a tube. *Phys. Fluids* 12, 2367–2371.
- Danckwerts, P.V., 1970. *Gas-Liquid Reactions*. McGraw-Hill, New York.
- Vandu, C.O., Liu, H., Krishna, R., 2005. Mass transfer from Taylor bubbles rising in single capillaries. *Chem. Eng. Sci.* 60, 6430–6437.
- Krauß, M., Rzehak, R., 2017. Reactive absorption of CO₂ in NaOH: detailed study of enhancement factor models. *Chem. Eng. Sci.* 166, 193–209.
- Vas Bhat, R.D., Kuipers, J.A.M., Versteeg, G.F., 2000. Mass transfer with complex chemical reactions in gas-liquid systems: Two-step reversible reactions with unit stoichiometric and kinetic orders. *Chem. Eng. J.* 76, 127–152.
- Pohorecki, R., Moniuk, W., 1988. Kinetics of reaction between carbon dioxide and hydroxyl ions in aqueous electrolyte solutions. *Chem. Eng. Sci.* 43, 1677–1684.
- Tsonopoulos, C., Coulson, D.M., Lawrence, B.I., 1976. Ionization constants of water pollutants. *J. Chem. Eng. Data* 21, 190–193.
- Edwards, T.J., Maurer, G., Newman, J., Prausnitz, J.M., 1978. Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes. *AIChE J.* 24, 966–976.
- Johnson, K.S., 1982. Carbon dioxide hydration and dehydration kinetics in seawater. *Limnol. Oceanogr.* 27, 849–855.