GHGT-12

Volume of fluid modeling of the reactive mass transfer of CO₂ into aqueous amine solutions in structured packed elements at micro-scale.

D. Sebastia-Saez, S. Gu*, P. Ranganathan

School of Energy, Environment and Agrifood, Cranfield University, Cranfield, MK43 0AL, United Kingdom.

Abstract

This article presents a CFD model to describe the interfacial reactive mass transfer that takes place between a gas phase and a falling liquid film within a structured packing reactor. The simulations encompass the hydrodynamics, physical mass transfer and reaction kinetics. Regarding hydrodynamics, the liquid misdistribution phenomenon is represented and compared to experimental data found in the literature. Physical mass transfer is also implemented and an analysis of the influence of several parameters (e.g. amine concentration, gas pressure, gas velocity, flow configuration and contact angle) is carried out. Finally, the reactive mass transfer characteristics of the MEA-CO₂ system are tested, showing the ability of the model to describe the values of the enhancement factor and the depletion of the solute in the bulk phase. The model is to be extended to meso-scale in the future to account for the performance of commercial structured packings.

1. Introduction

Fossil fuel consumption in the last century has increased the concentration of GHG (greenhouse gases) in the atmosphere, contributing to anthropogenic climate change. Moreover, energy generation in power plants is considered to be one of the most important sources of CO₂ emissions [1], being carbon capture and storage (CCS)
well suited to treat the low CO2 concentration values found in the flue gas generated at those facilities. CCS is the
technology that deals with trapping the CO2 from large point sources (i.e. such as power plants), its transport and
either its storage in appropriate geological formations or its use for enhanced oil recovery (EOR) [2]. Post-
combustion trapping with aqueous monoethanolamine solutions in structured packing reactors is the most accepted
among the different techniques available as it is a mature technology used over the last years in the chemical and
food industry [3, 4].

A post-combustion carbon capture plant consists of two columns: the absorber and the stripper. The input streams
to the absorber are the flue gas from the power plant and an aqueous amine solution (i.e. being MEA, MDEA and
TEA the most common substances used for this purpose). The absorber is filled with either a structured or a random
packing material, which ensures a high contact area per unit volume. The reactive mass transfer of CO2 takes place
with both fluids running in counter-current disposition. The output streams from the absorber are the clean flue gas
ready to be emitted to the atmosphere and the CO2-loaded amine solution, which enters the stripper to be
regenerated. Hot steam is applied in this second column to break the weak bonds between the amine and the CO2.
The regeneration process carries the highest energy penalty of the system, accounting for as much as 80% of the
total operational cost [5, 6]. The amine is thereafter recirculated to the absorber, closing the cycle. The final product
is an almost pure CO2 stream ready for the next stages of the CCS process.

CFD has become an important instrument in recent years to characterize multiphase flows occurring within
intricate geometries. The number of experiments can be limited by applying numerical techniques hence reducing
design costs [7]. CFD simulations are especially attractive in this field because of the difficulty in implanting
measurement probes between the metallic sheets that constitute the structured packing without interfering with the
flow patterns [8]. CFD analysis of multiphase flow within post-combustion absorption reactors is divided into three
scales (i.e. including macro-, meso- and micro-scale) as a result of the current computational capacity restrictions [9,
10]. At macro-scale, the whole reactor is modeled as a porous medium. The influence of geometrical features such as
walls, injectors, etc. in the flow patterns can be studied by this approach. The advection-diffusion equation [11] can
also be included in these models to study the spreading of the liquid. Meso-scale calculations utilize computational
domains whose dimensions are limited to several REUs (representative elementary unit). REUs are a repeating
geometrical unit that forms the structured packing material. Meso-scale focuses on the pressure drop characteristics
since it has been proven that the pressure loss per unit length for a small set of REUs is the same as for the whole
absorber [12, 13]. The simulations at this scale are performed only with the gas-phase, giving the dry pressure
characteristics. The results are corrected subsequently with experimental correlations, which take into account the
liquid holdup to calculate the wet pressure drop of the packing [7]. Micro-scale simulations are limited to
computational domains measuring a few centimeters to represent the gas-liquid interface usually by means of the
VOF method. Characteristics such as the liquid misdistribution phenomenon, which affects directly the absorbing
performance, can be assessed by this approach. Liquid misdistribution consists in the irregular distribution of the
liquid film, which results in partially wetted metallic plates. Accordingly, in practice, not all the surface of the
packing is actually available for mass exchange, reducing considerably the absorption capability of the process. The
magnitude of the liquid misdistribution depends on the ratio between the distortive (i.e. inertia) and cohesive (i.e.
surface tension) forces acting on the fluid, which is known as Weber number [14]. High values of the Weber number
imply a good spreading of the liquid, increasing the interfacial exchange area but also carrying a decline in the
contact time between fluids hence hindering the process. An optimal point taking into account both opposite effects
is postulated in our previous work [15]. Liquid misdistribution has been previously investigated experimentally by
Fourati et al. [16], who carried out its visualization by means of gamma ray tomography. Physical and reactive mass
transfer characteristics can also be checked by means of the micro-scale approach. However, the literature featuring
the simulation of reactive absorption systems is scarce and usually limited to 2D computational domains. Haelssig et
al. [17] studied the physical mass transfer characteristics of a water-ethanol mixture for falling liquid films in 2D
geometries. Haroun et al. [18] developed an in-house code called JADIM to account for the reactive mass transfer
performance on gas-liquid systems. The authors satisfactorily reproduced the concentration discontinuity near the
interface region and validated their model against the relationship between the enhancement factor and the Hatta
number presented by van Krevelen and Hoftijder [19]. Finally, the latest efforts in the modeling have been directed
to expand meso-scale simulations by also including gas-liquid interface tracking. Haroun et al. [20] reported results
about the liquid misdistribution phenomenon on large computational domains consisting of actual sections of Mellapak 250.X.

This work aims to contribute to fill the gap on CFD modeling of reactive mass transfer through a gas-liquid interface. The validation of the hydrodynamics in terms of the variation in wetted area as a function of the liquid injection velocity is accomplished by comparison with experimental data [14, 21, 22]. The results from the implementation of physical absorption are contrasted to the experimental results from Xu et al. [23]. Further validation is accomplished for the relationship between the Sherwood and the Reynolds number compared with theoretical and experimental correlations [24, 25, 18]. Higbie's penetration theory [26] is used to describe the physical mass transfer whereas the enhancement factors and specific mass source terms are implemented to account for the chemical behavior of the system. The results show a growing tendency on the enhancement factor as the concentration of monoethanolamine increases, which is in accordance with data found in the literature [27]. Also the consequence of a higher liquid load on the enhancement factor is assessed. The CO₂ concentration profiles within the liquid film are analyzed, highlighting the ability of the model to reproduce the depletion of the solute in the bulk liquid.

**Nomenclature**

<table>
<thead>
<tr>
<th>Latin symbols</th>
<th>Greek symbols</th>
<th>Subscripts</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>surface curvature [m⁻¹]</td>
<td>e</td>
</tr>
<tr>
<td>C</td>
<td>mass concentration [kg·m⁻³]</td>
<td>for</td>
</tr>
<tr>
<td>D</td>
<td>diffusivity [m²·s⁻¹]</td>
<td>g</td>
</tr>
<tr>
<td>F</td>
<td>volume fraction [-]</td>
<td>i</td>
</tr>
<tr>
<td>g</td>
<td>acceleration due to gravity [m·s⁻²]</td>
<td>l</td>
</tr>
<tr>
<td>K</td>
<td>molar reaction rate [m³·mol⁻¹·s⁻¹]</td>
<td>TOT</td>
</tr>
<tr>
<td>k</td>
<td>liquid-side mass transfer coefficient [m·s⁻¹]</td>
<td></td>
</tr>
</tbody>
</table>
2. Numerical methodology

ANSYS® Fluent v.14.0 is used to perform the present calculations. The finite volume method (FVM) is implemented in the software to solve the Navier-Stokes equations.

The mass conservation equation reads:

$$\nabla \cdot \vec{v} = 0$$  \hspace{1cm} (1)

Whereas the momentum conservation equation is:

$$\rho \left( \frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = -\nabla P + \mu \nabla^2 \vec{v} + \rho \vec{g} + \vec{f}$$  \hspace{1cm} (2)

In this work the generic body force \(\vec{f}\) accounts for the surface tension, which is modeled by the continuum surface force (CSF) theory [28]. The equation for the surface tension according to this model is:

$$\vec{f} = \sigma \frac{\rho \kappa \nabla F}{0.5 \left( \rho_f + \rho_g \right)}$$  \hspace{1cm} (3)

The assumptions of incompressibility and isothermal flow are taken. The interface between both phases is tracked by means of the volume of fluid method (VOF), which solves an additional transport equation for an auxiliary variable called volume fraction. A value for the volume fraction equal to 1 means that the cell is filled with liquid whereas if the value is equal to 0 then the cell is filled with gas. Values in between denote the gas-liquid interface, whose quality depends on the resolution of the mesh. The interface is rebuilt after the calculation by means of the Geo-reconstruct algorithm. The values of the viscosity and density are volume fraction-averaged.

The computational domain consists of a 6x5 cm² plate inclined 60° above the horizontal, which has been used to carry out the part of the study dealing with the hydrodynamics and the physical mass transfer characteristics. The geometry can be seen in Figure 1.

Figure 1 Detail of the computational domain and its mesh

Three different computational grids were tested (e.g. 1.0 x 10⁶, 1.2 x 10⁶, and 1.4 x 10⁶ cells) showing the independence of the results with respect to the mesh size. The values obtained are presented in Table 1.
Regarding the chemistry characteristics, mass source user-defined functions (UDF) characterizing the consumption and generation of reactants and products, respectively, were implemented in a smaller version of this geometry (i.e., 6x3 cm$^2$) in order to reduce the required wall time. The size of the mesh used in these cases was limited to 579,852 hexahedral elements.

The following table summarizes the numerical schemes used in the present work. The explicit method has been selected for the transient calculations as the surface tension has important effects. A variable time step has been set to ensure a quick convergence. The Courant-Friedrichs-Levy condition is fixed at a constant value of 0.5 [29].

<table>
<thead>
<tr>
<th>Variable scheme</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>PRESTO!</td>
</tr>
<tr>
<td>Momentum</td>
<td>Second order upwind</td>
</tr>
<tr>
<td>Pressure-velocity coupling</td>
<td>PISO</td>
</tr>
</tbody>
</table>

3. Theoretical background

Higbie’s penetration model [26] is implemented in this work to describe the interfacial physical mass transfer. The mass source term is included in the mass conservation as a UDF. Its equation reads:

$$S_{lg} = k_i \alpha C_i,_{TOT} (y_i^* - y_i)$$  \hspace{1cm} (4)

The driving force of the absorption process is then the concentration difference between the interface, which is considered to be saturated (i.e. and is denoted by the superscript $^*$), and the bulk liquid phase. The gas-side mass transfer coefficient is assumed to be neglected. The liquid-side mass transfer coefficient is calculated as:

$$k_i = 2 \sqrt{\frac{D_i}{\pi \tau}}$$  \hspace{1cm} (5)

The values of the solubility of both gases used in these simulations are calculated by means of the methodology presented by Penttilä et al. [30]. The diffusivity within the liquid phase is obtained from the Wilke-Chang equation [31]. The N$_2$O-CO$_2$ analogy is utilized, in the cases where a MEA solution is considered instead of water.

The equation for the exposure time is:

$$\tau = \frac{L_i}{v_i}$$  \hspace{1cm} (6)

Whereas the interfacial area is obtained as the gradient of the volume fraction in each particular cell:
The chemistry of the MEA-CO₂ system is described by the zwitterion mechanism [32, 33]. The carbon dioxide reacts with the amine to form a molecule called zwitterion, which in turn is transformed into a carbamate. The combination of carbon dioxide with hydroxide to form bicarbonate (i.e. equation 8) and that between MEA and CO₂ to form carbamate (i.e. equation 9) are finite rate reactions and can be implemented in the code with mass source UDFs. The rest of the reactions have an instantaneous behavior.

\[
CO_2 + OH^- \rightleftharpoons HCO_3^-
\]

(8)

\[
CO_2 + MEA + H_2O \rightleftharpoons MEACOO^- + H_3O^+
\]

(9)

\[
2H_2O \rightleftharpoons OH^- + H_3O^+
\]

(10)

\[
HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+
\]

(11)

\[
MEA + H_3O^+ \rightleftharpoons MEA^- + H_2O
\]

(12)

\[
MEACOO^- + H_2O \rightleftharpoons MEA + HCO_3^-
\]

(13)

There exists the consensus in the literature that the carbamate formation is the controlling step of the entire system whereas reaction (8) can be neglected because of its slow kinetics [34].

The importance of the reaction kinetics over the physical gas absorption rate can be measured by the Hatta number, which influences the enhancement on the absorption process that follows as a consequence of the existence of the chemical reaction. The Hatta number \( (Ha) \) for the carbamate formation reaction is calculated as [35]:

\[
Ha = \sqrt{\frac{K_{for}[MEA]D_{CO_2,j}}{k_i}}
\]

(14)

The square brackets in equation (14) denote molar concentration. Due to the fast kinetics of the reaction the assumption of equality between the Hatta number and the enhancement factor is taken [36]. The enhancement factor is the ratio between the rate of absorption with and without chemical reaction. According to the literature, the carbamate formation presents a second order irreversible kinetic behavior and its reaction rate can be written as:

\[
R = K_{for}[CO_2][MEA]
\]

(15)

The value of 24,984 m³·kmol⁻¹·s⁻¹ is used for the forward reaction rate [36].
4. Validation of the model

4.1. Hydrodynamics

The validation of the hydrodynamics was accomplished in terms of the relationship between the percentage of wetted area for pure water and the velocity profiles within the liquid film. The data obtained for the wetted area are compared to experimental results found in the literature [14, 22] and can be seen in Figure 2. The velocity profiles are compared to the theoretical predictions by Nusselt theory [37] for a 30 % wt. MEA-water mixture (Figure 3).

Figure 2 Percentage of wetted area vs. Reynolds number

Figure 3 Velocity profiles within the liquid film (30% wt. MEA)

Figure 4 shows the three different flow regimes observed depending on the value of the liquid injection velocity. The trickling flow (Figure 4a) corresponds to low velocity values, which develops as a consequence of the surface tension forces being predominant. More wetted area is found as the liquid velocity increases, which results in the rivulet flow (Figure 4b). Further increasing finally results in the whole metallic area covered by the liquid, which receives the name of full film flow (Figure 4c).
4.2. Physical mass transfer

The validation of the physical mass transfer characteristics of the O₂-water system is achieved by comparison with the Pigford model [24], the Zogg model [25] and the correlation reported by Haroun et al. [18]. The relationship between the Sherwood number and the Reynolds number presents the growing behavior observed in Figure 5a. Further validation is achieved by contrasting the mass fraction of the solute at the liquid outlet for a propane-toluene mixture (Figure 5b) [23].
5. Results

5.1. Effect of the liquid load on the absorption rate

Figure 6 shows the effect of the liquid load on the net oxygen absorption rate, which is calculated as the product of the average mass fraction of the solute at the outlet times the mass flow rate of liquid. It can be seen in the figure that the oxygen absorption rate increases with the liquid load by virtue of the higher amount of interfacial area between both fluids. However, it reaches a maximum point that matches the transition to full film flow. The reason for the decrease in the oxygen absorption rate beyond this point is that the contact time between phases is reduced as the velocity of the liquid phase increases.

Figure 6 Effect of liquid load on the oxygen absorption rate

5.2. Effect of liquid viscosity, gas pressure and velocity, flow configuration and contact angles.

Figure 7 shows the influence of several parameters on the oxygen mass absorption rate. The liquid viscosity of the fluid varies considering the MEA percentage. The assumption of a mass weighted mixing law has been taken in these calculations. The influence of the liquid viscosity over the solubility has been neglected [38]. The case of pure water is compared to two common amine solutions found in industry (i.e. 30% and 40% wt. MEA). It can be observed in Figure 7a that the rate of physical absorption diminishes substantially as the MEA mass fraction increases, which is due to the fact that a higher viscosity hinders the gas diffusion process. Gas pressure affects the absorption through the value of solubility via Henry's law (Figure 7b). Three relative gas pressure values are tested in this work (i.e. atmospheric pressure, 0.5 atm and 1 atm). A substantial improvement of up to 60% in the oxygen absorption rate has been reported when the pressure is increased from 0 atm to 0.5 atm relative pressure. Also the gas velocity and the flow configuration can influence the amount of gas transferred from the gas to the liquid (Figure 7c). Velocity profiles by means of UDFs have been included at the gas inlet to control its velocity. The results show how the co-current configuration tends to spread the liquid over the metallic plate, which boosts the amount of exchange area resulting in enhanced mass transfer. The counter-current configuration tends to hold the liquid in the vicinity of the inlet, hampering the liquid spreading process. Contact angles are the result of the balance between the internal cohesion of the molecules forming the liquid phase and the adhesion between the fluid and the solid surface. The calculations show that a better adhesion of the liquid to the solid surface results in a better wetting, increasing the interfacial surface (Figure 8). Therefore, adhesion can be also considered as a distortive force whereas cohesion has the same effect surface tension has in the analysis of the amount of wetted area as a function of the Weber number [39]. The values of the contact angle tested are 60°, 70°, 80°, 100°, and 110°. The importance
A good material choice is thus highlighted since adhesion forces depend on both the characteristics of the fluid and the solid material that forms the structured packing.

Figure 7 Influence of flow parameters in the physical absorption performance: (a) effect of liquid viscosity (b) effect of gas pressure (c) effect of gas velocity and flow configuration

Figure 8 Flow patterns as a function of the contact angle: (a) 100° and (b) 70°
5.3. Chemical absorption modeling

The analysis of the chemical absorption modeling is discussed in this section. The variation of the enhancement factor as a function of the MEA mass fraction is appraised in Figure 9. The increasing behavior observed is explained by means of the definition of the Hatta number, which depends directly on the squared root of the amine concentration. The assumption of the enhancement factor being equal to the Hatta number is taken by virtue of the second order irreversible behavior of the reaction [36]. The tendency can also be explained with the kinetic theory, which says that the probability of collision between the reactant molecules to trigger the reaction is higher as the MEA concentration on the liquid phase increases. The same trend has been observed in the literature too [27]. The influence of the liquid load can also be checked in the same figure. Bigger liquid loads give lower enhancement factors as a general behavior. A reduction of about 8% has been reported as the liquid injection velocity increases from 38 cm·s⁻¹ to 45 cm·s⁻¹ due mainly to the bigger liquid side mass transfer coefficient.

The concentration profiles for the carbon dioxide can be observed in Figure 10, which shows the values obtained for the three amine solutions tested.
It has been observed that the concentration is higher for the most diluted aqueous solution (i.e. 30% wt. MEA). The bigger diffusivity values and reaction rates observed for low viscosities explain this trend. Figure 10 also shows the penetration depth of the carbon dioxide on the liquid film, which has an approximate value of 0.1 mm whereas the total liquid film thickness is around 0.7 mm. Therefore, it has been proven that the model is capable of reproducing the depletion of the solute in the bulk liquid phase ascribed to the high value of the Hatta number. Both physical and reactive absorption are compared under the same flow characteristics in Figure 11. The physical absorption is accomplished by disabling the consumption mass source terms due to the chemical reaction.

Figure 11 still shows higher concentrations in the vicinity of the interface and the profile described by Higbie’s penetration theory is well reproduced. Also, In contrast to the reactive case, the carbon dioxide is able to reach the bulk of the liquid, which highlights the effectiveness of the model to represent the fast kinetics of the CO$_2$-MEA system.

6. Conclusions

This work presents a complete micro-scale CFD model for the reactive mass transfer taking place within structured packing reactors. The results presented encompass the hydrodynamics, the interfacial physical mass transfer and the
reaction kinetics characteristics. Regarding the hydrodynamics the liquid misdistribution effect and velocity profiles are represented by means of the VOF method and validated against experimental data. Also, the influence of several parameters (i.e. such as liquid viscosity, gas pressure, gas velocity, flow configuration, and contact angles) on the physical mass transfer performance is assessed. Finally, the reaction kinetics of the CO2-MEA system is implemented, giving expected results for the enhancement factor and featuring a good portrayal of the depletion of the solute in the bulk liquid. The model can be exported to meso-scale in the future to optimize actual sections of commercial structured packings.

Acknowledgements

The authors would like to acknowledge the financial support of the UK CCS Research Centre (www.ukccsrc.ac.uk) in carrying out this work. The UKCCSRC is funded by the EPSRC as part of the RCUK Energy Programme. The authors would also like to acknowledge the financial support from the UK Engineering and Physical Sciences Research Council (EPSRC) project grant: EP/J020184/1 and FP7 Marie Curie iComFluid project grant: 312261

References


