



# Dynamic Modelling of the Reactive Absorption of CO<sub>2</sub> in Ionic Liquids and its Effect on the Mass Transfer and Fluid Viscosity

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The main objective of this work is to develop a suitable fluid dynamic model of a CO<sub>2</sub> absorption system using ionic liquids as solvent giving special emphasis in the impact of the viscosity of the solvent on the reactor designing issues such as overall removal capacity, reactor geometry and power required. A very important drawback of ionic liquids is the increase in viscosity during the CO<sub>2</sub> absorption process which results in a decrease of the overall mass transfer rate and an increase in the power required for pumping and mixing. In order to establish the main mass transfer and hydrodynamic parameters and in particular the impact of the viscosity in the system, a two-dimensional computational fluid dynamic (CFD) simulation was carried out to model a simple gas absorption bubble column with one inlet gas feed. To model the interface tracking, the level set method was used. Meanwhile the laminar and non stationary hypothesis was applied for the liquid and gas phases. The CFD software COMSOL 4.2, which employs the finite elements method to discretized the Navier Stokes and Mass Transfer fluid flow Equations, was used to simulate and analysing the obtained results from simulations. The results show an increase of the overall mean viscosity over the time due to the CO<sub>2</sub> diffusion in the liquid, meanwhile the spatial distribution of the viscosity was very homogeneous due to the high mixing capacity of the bubble column. However there was a slight gradient in the bottom of the reactor.

## 1. Introduction

Since the use of fossil fuels has been massive at a world-wide level, a number of environmental issues have begun to be known in a great number of social aspects. CO<sub>2</sub> is one of the main products of fuel combustion, and is also one of the main greenhouse gases in the atmosphere, thus the continuous increase in its atmospheric concentration has caused a great concern in the scientific community because of its environmental hazard and its humanitarian implications (Yu et al. 2010). Therefore, following the 1997 Kyoto Protocol, the European Union has set a target of 20 % reduction of CO<sub>2</sub> emission by the year 2020 (Khan et al., 2011). To meet this goal, a significant reduction in the CO<sub>2</sub> releases from fossil fuel will be required during the next years. This can be achieved by adopting an effective strategy for carbon capture and storage (CCS) (Khan et al., 2011), which indirectly recognizes the importance of fossil fuels to society and that CO<sub>2</sub> is an essential product of its utilization. The proposed approach focus in the possibility to explore synergic use of different chemical technological tools which are: the use of novel task specific ionic liquid (TSILs) as solvent and electrochemical promotion of catalytic reduction reaction, being thus in line with the concept of process intensification (the enhancement of phenomena approach). Ionic Liquids (IL) conform a wide group of salts, which are

liquids at room temperature, have low vapour pressure, high ionic conductivity, wide electrochemical potential window, and thermal stability (Wasserscheid, 2008). However, the use of IL for industrial CO<sub>2</sub> depletion has a series of technical and economic issues that must be solved if this strategy is to be implemented. One of these problems is the high viscosity of the IL and its consequence during the absorption process; with the result of an increase in the necessary energy for pumping (Wappel et al. 2010).

The viscosity and other properties of the IL may be modified by changing the substitute group in the cations and anions (Galán Sánchez et al., 2007). In addition, the same effect it may be achieved by mixing the IL with water. However, just some ILs are soluble in water (Galán Sánchez et al., 2011), and the physical-chemical properties of the solvent may be affected in a negative way. During the gas absorption process, the viscosity increase may be controlled by a continuous removal of the solvent before the viscosity increases in a decontrolled way.

A deep study on the available literature shows that there are just a few studies on reactor designs for gas removal based on IL, in which the viscosity control is based through the fluid hydrodynamics inside the reactor. An important exception to this concept is the design created by Luis et al. (2009), in which semi permeable ceramic membranes were used for the absorption of SO<sub>2</sub>.

This design allows the IL be separated partially in the gas phase in a way that the liquid follows circulating at the same time that the solute is absorbed. On this way, the viscosity in the system is indirectly under control. The great majority of the studies in this field are just focused on understand the solute mass transfer, concentrations profiles, velocity fields, gas hold up, and the pressure drop for conventional reactors of the type bubble column (Rigopoulos and Jones, 2003), packed bed reactor (Khan et al., 2011; Liu et al. 2006; Raynal and Royon-Lebeaud, 2007; Ghaemi et al., 2009; Raynal, 2009; Ben Rayana et al. 2009), stirred tank reactor (Kurnia et al., 2009), and falling film contactor (Chasanis et al. 2010). In addition, most of these studies have been developed in a batch regime.

Many of the studies made in the last years regarding the CO<sub>2</sub> removal by means of ILs are developed in one spatial dimension (1D) (Khan et al., 2011; Zhang et al. 2007; Ghaemi et al., 2009; Luis et al., 2009; Galán Sánchez et al., 2011). However, one dimensional models shows evident limitations when viscosity is a non-steady variable and therefore, hydrodynamics is a determinant factor in the absorption process. For all the reasons exposed, this work is focused in the development of mathematical models of the CO<sub>2</sub> absorption process into ILs for the CCC process. The models are based on the conservation of momentum, heat, mass and chemical reaction equations and describe the CO<sub>2</sub> concentration profiles in the liquid phase as a function of both: location and time. Of interest is our focus on the study of the effect of the absorption process on the viscosity changes during the absorption progression and its effects on the mass transfer development. In this work we will show the results of the first CFD simulations predicting the effect of the viscosity on the absorption process and mass transfer of CO<sub>2</sub> in an IL. There is very few theoretical and experimental investigations on CO<sub>2</sub> absorption in ILs particularly applied to bubble column systems, one is the work done by Wang et al. (2010), whose used the CFD software FLUENT to simulate the system using the population balance model to describe the bubbly flow, however, they do not studied the effect of viscosity in the mass transfer and overall performance of the system.

In order to determine the hydrodynamic and mass transfer behaviour of a CO<sub>2</sub> absorption column using IL as solvent and considering the viscosity of the solvent as a process dependent parameter; CFD simulations was carried out to estimate the impact of such property in the overall performance of the system. A simplified two-dimensional model was developed which consider the liquid solvent (IL) as a Newtonian fluid, for which its viscosity depends only on the CO<sub>2</sub> concentration in the liquid phase. The laminar, isothermal, and non stationary hypothesis for both phases was applied. A computational mesh of 3374 triangular cells and the PARDISO solver was used utilizing a time step of 0.003 s.

## 2. Materials and methods

The general assumptions for the mathematical model used for the entire domain are of a laminar, incompressible and isothermal flow. The governing continuity, momentum and mass transport equations for the two-phase incompressible fluid flow of a liquid-gas mixture for unsteady conditions are as follows:

$$\nabla \cdot \bar{\mathbf{u}} = 0 \quad (1)$$

$$\bar{\mathbf{u}} \cdot \nabla(\bar{\mathbf{u}}) = -\frac{1}{\rho} \nabla p + \frac{1}{\rho} \nabla \bar{\boldsymbol{\tau}} + \mathbf{g} \quad (2)$$

where  $\rho$  is the fluid density,  $u$  is the fluid velocity,  $g$  is the gravity acceleration,  $p$  is the fluid pressure and  $\boldsymbol{\tau}$  is the stress tensor due to viscous forces. The source term  $F$ , includes the volumetric buoyancy force, due to the density difference between the gas and the liquid and the surface tension effect.

$$\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = \mathbf{F} \quad (3)$$

The level-set method was introduced by Osher and Sethian, 1988, for incompressible two phase flow. The motion of the interface is characterized through the advection function ( $\varphi$ ) of the level-set function as follows:

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = 0 \quad (4)$$

$$\rho = \rho_c H(\phi) + \rho_d (1 - H(\phi)) \quad (5)$$

and

$$\mu = \mu_c H(\phi) + \mu_d (1 - H(\phi)) \quad (6)$$

Where  $H(\varphi)$  is a smooth heavy side function, the subscripts  $c$  and  $d$  represents the continuous phase and the dispersed phase, respectively.  $H(\varphi)$  is defined as:

$$H(\phi) = \frac{1 + \tanh\left(-\frac{\phi}{n}\right)}{2} \quad (7)$$

The width of the transition interface is controlled by the parameter  $n$ . The two components of the body force term can be calculated as:

$$F_x = \sigma k \delta(\phi) n_x \quad (8)$$

and

$$F_y = \sigma k \delta(\phi) n_y + \rho g \quad (10)$$

Where  $\sigma$  is the surface tension,  $k$  is interfacial curvature, and  $n_x$  and  $n_y$  are the components of the unit normal vector at the interface pointing, from the dispersed phase to the continuous phase. The delta function ( $\delta(\varphi)$ ) is an smoothed function (dirac delta) that ensures that the surface tension is applied only at the interface. The unit vector ( $n$ ) normal to the interface can be written as follows:

$$n = \frac{\nabla \phi}{|\nabla \phi|} \quad (11)$$

$$K = \nabla \cdot \frac{\nabla \phi}{|\nabla \phi|} \quad (12)$$

The interfacial mass transfer is implemented as an additional source-term into the mass transfer equations. The concentration in the interface is modelled through the two film theory which considers the thermodynamic equilibrium of the chemical species at the interface as follow:

$$\frac{\partial C_L}{\partial t} + \vec{u} \cdot \nabla C_L = \nabla(D_L \nabla C_L) \alpha_2 \left( C_L - \frac{C_L}{H_D} \right) \quad (13)$$

In our model, the value of  $\alpha$  is fixed to 0.2 and  $H_d$  to 1,101.26. The control of the position of the boundary is based on the  $\varphi$  local values and applying a delta Dirac function to limiting the position of the boundary to the interface. In order to model the non-constant solvent viscosity, a linear dependence from the solute liquid concentration is proposed which is describes as follows:

$$\mu = 0.0604438 + 0.003328 * c \quad (14)$$

Where  $c$  is the solute concentration in the liquid face.

### 2.1 Model implementation

The reactor has a height of 28.5 mm and width of 10 mm. The bottom inlet gas feed has a diameter of 2 mm and a constant gas feed velocity of 0.01 m/s with a concentration of CO<sub>2</sub> of 2 % mol. The properties of the liquid phase are 1,193.7 kg/m<sup>3</sup> for the density and for the gas phase: 1.204 kg/m<sup>3</sup> and 1.78×10<sup>-5</sup> kg/(m·s), for density and dynamic viscosity respectively. The diffusion coefficient is 9.62\*10<sup>-11</sup> m<sup>2</sup>/s and surface tension is 42.8 mN/m.

### 2.2 Numerical details and boundary conditions

The COMSOL 4.2 CFD software was used for all the simulations; which software uses the finite element method for approximating partial differential equations defining the mathematical model. Both the geometry and the computational mesh were created in COMSOL. Different three-dimensional grids were tested and a final hybrid mesh of 3,774 tetrahedral cells was used. For the purpose of modelling the interface tracking, the level set approach was used, which solves the momentum equations for the entire domain. The system was defined as non stationary and the total time for the simulations was 44 s. A direct PARDISO solver was used for all simulations. Convergence was achieve when all normalized. Residuals of velocity and concentration reached values smaller than 10<sup>-3</sup>. Simulations were performed on a HP Workstation with 4 Intel cores and 16 GB RAM. The CPU time for 1 s of simulation was 2,472 s. In order to ensure stability, in our work the value of time step was fixed of 0.0001 s. The maximum number of iterations is reached when the relative tolerance exceeds 0.001 with respect of all variables. The upper surface of the liquid (free surface) was defined as a zero pressure outlet free of shear stress. A non slip condition was used for the walls and a constant inlet gas velocity of 0.01 m/s was specified. The initial interface was settled at the gas inlet.

## 3. Results

The computational mesh is depicted in figure 1-a. The number of elements is 3,774 The element size ranges between 0.33 and 0.49 mm. It was not necessary to refine the mesh in the zones with high. The volume of fluid fraction at  $t = 0$  s,  $t = 0.4$  s,  $t = 1$  s and 1.2 are shown in the Figure 1 (b, c, d, e). The phases are identified by the colors black (gas) and white (liquid). As we can see, bubble suffers a shrink in the z direction and reaches a diameter between 6 and 7 mm, however, due to high viscosity of the solution, the bubbles do not suffer split.

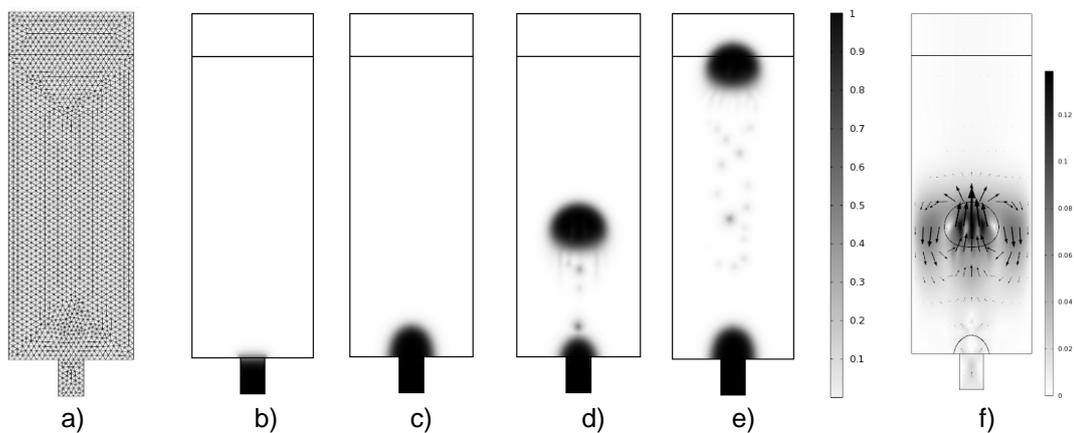


Figure 1: Computational grid a) volume fraction of gas face b)  $t = 0$  s, c)  $t = 0.4$  s, d)  $t = 1.0$  s, e)  $t = 1.2$  s and a f) Contour and vector plot of the velocity field. Legend units: m/s

Analyzing the velocity magnitude field, it is possible to see a high relative velocity symmetric shape near the bubble, which is part consequence of the distance from the reactor wall, as we can see in Figure 1f. The maximum velocity reached for a single bubble is almost 0.142 m/s at time 1.2 s. The concentration of the solute reaches almost 0.5 mol/m<sup>3</sup> near the gas interface during the first seconds. There is a slight gradient of concentration across the reactor during the first seconds.

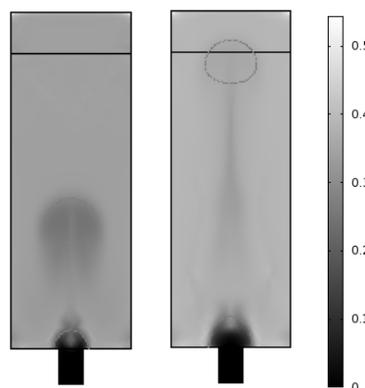


Figure 2. Contour plot of the concentration of the solute at time = 1 (left) and 1.2 s (right). Legend units: mol/m<sup>3</sup>

The maximum viscosity values inside the reactor during the 14 analysed seconds, starts with 0.0607 Pa.s at the beginning of the process and reaches 0.066 Pa.s at the end, which represents an increase of 1.6 % during 14 s.

#### 4. Conclusions

A simple CFD model was carried out to simulate a bubble column reactor for CO<sub>2</sub> absorption in ionic liquids. To carry out the simulations, the CFD software COMSOL 4.2 was used. The results show an increase of the overall mean viscosity over the time due to the CO<sub>2</sub> diffusion in the liquid, meanwhile the spatial distribution of the viscosity was very homogeneous due to the high mixing capacity of the bubble column. However there was a slight gradient in the bottom of the reactor. The next steps of this work involve the increase of the size of the reactor and a deeper analysis of the performance of the reactor at different process conditions and a further model validation with a laboratory scale bubble column.

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