Meso-scale CFD Modelling of CO2 Capture by Aqueous Ammonia Part I: Modeling

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Abstract. This paper reports numerical modelling and simulation of carbon dioxide capture from flue gases by aqueous ammonia solution as an absorbent. The simulation of the complex flows is mainly for the low efficiency of the present post-combustion capture technology, which includes a countercurrent two-phase flow considering chemical reaction between CO2 and NH3 solution in representative elementary units (REU) of structured packed column. Then, we compared the CO2 absorption between two REUs model and single REU model, the results show that more contact time means higher absorption rate. Furthermore, the feasibility of the model is checked over different operating parameters in the Part II. Based on the simulation, we can achieve the optimized design to the process parameters.

Introduction

Fossil fuels based energy consumption has been growing rapidly and driven by the expansion of the global economy and industrialization. Power generation from fossil fuel-fired power plants (e.g. coal and natural gas) is the largest source of CO2 emissions [1], so the reduction of CO2 emission from the power generation will play an essential part to combat the global warming. Intergovernmental Panel on Climate Change (IPCC) describes in 2005 that Carbon Capture and Storage technology (CCS) is expected to sharply reduce the emission of greenhouse gases [2]. CCS consists of separation of CO2 from industrial and energy-related sources and transportation of CO2 to safe and long-term storage sites. There are three major approaches for CO2 capture: namely post-combustion capture, pre-combustion capture and oxy-fuel process [3]. Post-combustion capture seems to be more acceptable as a retrofit option to existing plants compared to the other two approaches. A number of technologies have been developed with post-combustion capture. Chemical absorption using aqueous alkanolamine solutions, including monoethanolamine (MEA) [4] and aqueous ammonia, in packed columns are most applied in power plants [5]. A typical absorption process is shown in Fig. 1 [6]. The cooled flue gas encounters the lean solvent in the absorber. The scrubbed gas is then water washed and vented to the atmosphere. The rich solvent is heated in a cross heat exchanger by regenerated lean solvent from the stripper. It is subsequently pumped to the top of the stripper where it is regenerated at elevated temperatures. Heat is supplied via the reboiler which is the major energy penalty of the process. The regenerated solvent is then pumped back to the absorber via the cross heat exchanger to reduce the temperature.
Despite of continuous progress made in recent decades, CO$_2$ capture is still extremely expensive and could reduce the overall efficiency of the power cycle by approximately 30%. The use of CFD to simulate the carbon capture process offers a very cost-effective method to optimize operating conditions and reactor designs, which leads to the cost reduction and performance enhancement of the processes. CFD has been used to study the multiphase flows inside structured packing of the capture reactor in literature. However, the available computational capacity is limited and the study of post-combustion absorbers is divided in three different scales depending on the aspect to be evaluated: micro-scale, meso-scale and macro-scale [7]. In micro-scale CFD simulations, the gas-liquid flows in packing sheets are studied using the volume of fluid (VOF) method. Meso-scale CFD simulations use a small set of representative elementary units or REU (i.e. a repeating geometrical pattern formed by the metal sheets) to study the gas–liquid flow characteristics. Finally macro-scale simulations are performed for the whole absorption column using results from the previous scales as input data.

Hodson et al. [8] presented a micro-scale simulation of the flow pattern of a vapor phase in a packed column. Van Gulijk [9] demonstrated a simplified “Toblerone” model of a packing sheet to study the transversal dispersion in structured packing. Petre et al. [10,11] represented the structured packing as a combination of four representative elementary three-dimensional units (REU) with hydrodynamics and pressure drop in each REU using CFD. Gao et al. [12] studied the flow of a liquid phase in structured packing by tracking the free surface of the liquid using the volume-of-fluid (VOF) method in the two-dimensional model. Raynal et al. [13] were able to successfully estimate the thickness of the liquid film and consequently the liquid holdup in a structured packing. Mahr and Mewes [14] proposed a model for two-phase flow in structured packing columns and calculated the pressure drop in the packing at different angles.

Even though, few studies on different scales of CO$_2$ capture reactors are reported in literature, current CFD multi-phase models are limited to predict gas-liquid flow in packing units, without considering absorption and reactions. It is still challenging to model large scale reactors with detailed gas–liquid interactions on internal and column walls.

Periodic modeling has been applied to a variety of different packing arrangements by a number of studies [6,15,16]. This method allows CFD simulations to be performed on small representative elementary units (REU) which can focus on specific regions. In this paper, we use CFD to simulate CO$_2$ mass transfer along with chemical reaction in terms of carbon dioxide absorption rate in REU of structured packing.

**CFD Modelling**

**Mathematical Equations**

In this study, the fluid dynamics of gas-liquid flows is calculated using the two-fluid Eulerian method. In order to describe the coexistence of different phases in the flow the concept of volumetric fraction is introduced. The volume fractions for all the phases have to sum up to unity.
\[ \sum \alpha_k = 1. \]

Conservation equations are formed for each phase separately. The equation of mass conservation for \( k \)th phase takes the form:

**Conservation of mass:**

\[
\frac{\partial (\alpha_k \rho_k)}{\partial t} + \nabla \cdot (\alpha_k \rho_k \mathbf{u}_k) = S_k
\]

(2)

**Conservation of momentum:**

\[
\frac{\partial (\alpha_k \rho_k \mathbf{u}_k)}{\partial t} + \nabla (\alpha_k \rho_k \mathbf{u}_k \cdot \mathbf{u}_k) = -\alpha_k \nabla p + \nabla^2 (\alpha_k \mu_k \mathbf{u}_k) + \alpha_k \rho_k \mathbf{g}_k + \mathbf{F}_k
\]

(3)

**Conservation of energy:**

\[
\frac{\partial (\alpha_k \rho_k h_k)}{\partial t} + \nabla \cdot (\alpha_k \rho_k \mathbf{u}_k h_k) = \alpha_k \frac{\partial p}{\partial t} + \nabla \cdot (\lambda_k \nabla T_k) + Q_k + S_{e,k}
\]

(4)

Where \( \mathbf{u}_k \) is the velocity vector, \( \rho_k \) phase density and \( S_k \) is a mass source term corresponding to species production/destruction due to chemical reaction.

The term \( p \) in Eq. 3 is the static pressure shared by all phases, \( \mu_k \) stands for dynamic viscosity, \( \mathbf{g}_k \) is the gravity vector and \( \mathbf{F}_k \) describes an interaction force between phases.

The term \( h_k \) in Eq. 4 is the specific enthalpy of the \( k \)th species, \( \lambda_k \) stands for thermal conductivity, \( Q_k \) is the intensity of heat exchange between phases and \( S_{e,k} \) is the enthalpy source term due to chemical reaction.

**Turbulence model:**

The turbulence model for gas-liquid flow is based on Newtonian fluid, incompressible liquid and ideal gas. The standard \( k-\varepsilon \) turbulent model is used to calculate the liquid phase turbulence. The equations for the turbulent kinetic energy \( k \) and dissipation rate \( \varepsilon \) are:

\[
\frac{\partial (\rho k)}{\partial t} + \frac{\partial (\rho k \mathbf{u}_i)}{\partial x_i} = \frac{\partial}{\partial x_j} \left[ \left( \mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] + G_k - \rho \varepsilon
\]

(5)

\[
\frac{\partial (\rho \varepsilon)}{\partial t} + \frac{\partial (\rho \varepsilon \mathbf{u}_i)}{\partial x_i} = \frac{\partial}{\partial x_j} \left[ \left( \mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_j} \right] + \frac{C_{1\varepsilon}}{k} G_k - \frac{C_{2\varepsilon}}{k} \rho \frac{\varepsilon^2}{k}
\]

(6)

Where model constants are: \( C_{1\varepsilon}=1.44, C_{2\varepsilon}=1.92, \sigma_k=1.0, \sigma_\varepsilon=1.3 \).

**Chemical composition of the conservation equations:**

For the \( i \)th species in multiphase flow, chemical composition of the conservation equation takes in the following form:

\[
\frac{\partial}{\partial t} \left( \alpha_i \rho_i Y_{i,k} \right) + \nabla \cdot \left( \alpha_i \rho_i \mathbf{u}_k Y_{i,k} \right) = -\nabla \cdot \left( \alpha_i \mathbf{J}_{i,k} \right) + R_i + S_i
\]

(7)

Where \( Y_{i,k} \) represents the mass fraction of \( i \)th species, \( R_i \) is the chemical reaction rate, and \( \mathbf{J}_{i,k} \) is the diffusion flux for species \( i \). According to Fick’s law, the diffusion flux can be written as:

\[
\mathbf{J}_{i,k} = \alpha_i \rho_k D_{i,m} \nabla Y_{i,k} - D_{i,T} \frac{\nabla T}{T}
\]

(8)

Where \( D_{i,m} \) and \( D_{i,T} \) represent the mass and thermal diffusion coefficients of the \( i \)th species in the mixture respectively.

The term \( S_i \) in Eq. 7 represents the source term for the species \( i \). Due to mass transfer between the
bulk and interfacial concentrations, the interfacial concentration of species can be calculated using Henry’s Law as:

\[ Y_{G,j}^f = H e Y_{L,j}^f. \]  \hspace{1cm} (9)

Where \( He \) is the Henry’s law constant.

**Periodic Element Construction**

The commercial Montz-pak B1-250.45 packing uses unperforated corrugated metal sheets which are positioned with an inclination angle of 45°. Geometric properties of packing include a base width of 0.0225m, height of 0.012m, surface area of 244 m²/m³ and porosity of 98%. A periodic model of an REU is three-dimensional with unstructured mesh (cell size of 1mm) as shown in Fig. 2.

![Image of periodic element construction](image)

(a) Structured element unit  \hspace{1cm} (b) Meshing unit

**Figure 2. REU with 45° inclination angle.**

**Chemical Reactions**

The process of aqueous ammonia absorption of \( \text{CO}_2 \) involves complicated chemical gas-liquid reactions including:

\[ \text{CO}_2 + 2\text{NH}_3 = \text{NH}_2\text{COONH}_4. \]  \hspace{1cm} (10)

\[ \text{NH}_2\text{COONH}_4 + \text{H}_2\text{O} = \text{NH}_4\text{HCO}_3 + \text{NH}_3. \]  \hspace{1cm} (11)

\[ \text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4\text{OH}. \]  \hspace{1cm} (12)

\[ \text{NH}_4\text{HCO}_3 + \text{NH}_4\text{OH} = (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}. \]  \hspace{1cm} (13)

\[ (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = 2\text{NH}_4\text{HCO}_3. \]  \hspace{1cm} (14)

The above reactions are reversible and can be simplified as:

\[ \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} \xrightarrow{k_1} \text{NH}_4\text{HCO}_3. \]  \hspace{1cm} (15)

The chemistry of Eq. 15 was modelled by laminar finite-rate model using Arrhenius expression to calculate the forward reaction rate constant \( k_1 \):

\[ k_1 = A e^{-E_r/RT}. \]  \hspace{1cm} (16)

Where \( A \) represents pre-exponential factor \( (2.4 \times 10^5 \text{mol}^{-1}\text{•dm}^3\text{•s}^{-1}) \) and \( E_r \) represents activation energy \( (26.73 \text{kJ/mol}) \).
Boundary conditions

The simulations are non-steady state with time step of 0.001s. Atmospheric pressure was used and the effect of gravity was considered in the Y-axis negative direction. Inlet and outlet boundary conditions are shown in Fig. 3. The inlet for gas phase is set at velocity of $V_g = 0.737 \text{ m/s}$ with flow rate of $Q_g = 3000 \text{ m}^3/\text{h}$ (column diameter of 1.2m), along the Y-axis direction into the packing material. The gas is a mixture of CO$_2$ and N$_2$ with CO$_2$ mass fraction of 0.14. The inlet for liquid phase is set as $V_l = 0.00737 \text{ m/s}$, along the Y-axis negative direction into the packing material. The mole fraction of NH$_3$ at inlet is 0.05. The outlet for gas-liquid mixture is set as pressure boundary. No slip wall is used and the operating temperature is 300K. ANSYSs ICEM CFD was used to mesh the model of REU and ANSYS Fluent 14.5 was used to compute the hydrodynamics and mass transfer along with species transport for simulating the reactive absorption process.

Model Analysis

Single REU Model

A single REU for the capture process is modelled for 1.5s. Fig. 4 shows the mole fraction of NH$_4$HCO$_3$ on the surface of structured packing at different time. It shows that the chemical reaction occurs in the packing element, the producer of NH$_4$HCO$_3$ increases to the maximum level at 0.3s and then gradually decreases to a constant value as time progresses. The increase of NH$_4$HCO$_3$ is driven by the rate of reaction. From the simulation results, CO$_2$ absorption rate is calculated using inlet CO$_2$ mole fraction and final mole fraction of NH$_4$HCO$_3$. The CO$_2$ inlet mass fraction is 0.14, representing the mole fraction of 0.094. The mole fraction of NH$_4$HCO$_3$ on the surface in the finally state is $1.780 \times 10^{-7}$. Therefore, CO$_2$ absorption rate in the single REU model can be found as: $71.780 \times 0.00019\% = 0.00019\%$. 

![Figure 3. Boundary conditions of REU.](image-url)
The profiles of produced \( \text{NH}_4\text{HCO}_3 \) concentration during chemical reaction on the surface of structured packing are shown in Fig. 5. It is found that the concentration distribution of \( \text{NH}_4\text{HCO}_3 \) on the upper surface increases with time. This behavior can be explained as that due to buoyancy the gas tends to move upwards and accumulate at the top surface, accumulated gas increases as time increases, which undergoes the higher mass transfer, followed by the chemical reaction.

Two REUs Model

To examine in what extent a REU represents the full absorption process, two REUs are modelled in a vertical arrangement as shown in Fig. 6. The mesh size and boundary conditions are the same as the single REU described in the section of Boundary conditions. The result in Fig. 7 demonstrates the same trend for the mole fraction of \( \text{NH}_4\text{HCO}_3 \) as the single REU result in Fig. 4. The peak for the mole fraction of \( \text{NH}_4\text{HCO}_3 \) is delayed to 0.5s while the \( \text{CO}_2 \) absorption rate increases to 0.00054%,

![Figure 4](image)

![Figure 5](image)

![Figure 6](image)

![Figure 7](image)
which is 60% higher than that of the single REU. This is due to more contact between the gas and the liquid for two REUs, which results in may be due to fact that the volume space of the two REUs model is larger than that of in a single model which leads to higher degree of chemical reactions.

(a) Structured element unit  
(b) Meshing unit

Figure 6. REU with two packing elements.

Figure 7. The mole fraction of NH₄HCO₃ on the surface of structured packing at different time.

The profiles of NH₄HCO₃ concentration on the surface of structured packing at the gas velocity of 0.737 m/s are shown in Fig.8. The results in Fig.8 show that the NH₄HCO₃ concentration distribution is higher at the top surface of packing and it increases with increasing time as the single REU predictions.
Fig. 9 shows concentration distribution of NH$_4$HCO$_3$ on the surface of structured packing with different gas flow rates. It is found that NH$_4$HCO$_3$ concentration on lower surface improves with decrease of gas flow rate. This can be due to fact that decreasing gas flow rate can help increase the gas-liquid contact area, which leads to a higher degree of chemical reaction.

Figure 8. The profiles of NH$_4$HCO$_3$ concentration distribution on the surface of structured packing at different time.
Conclusion

Meso-scale CFD simulation is carried out for REU of Montz-Pak B1-250.45 commercial structured packing. The results show higher CO₂ absorption with two REUs than single REU due to longer contact time for gas and liquid phases.

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