

Hydrodynamic-Analogy-Based Modelling of CO₂ Capture by Aqueous Monoethanolamine

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Modelling of gas/vapour-liquid separation processes usually requires experimentally determined parameters, e.g. mass transfer coefficients that cannot be determined without expensive experimental work. A novel modelling approach based on hydrodynamic analogies (HA) has recently been developed and successfully tested for distillation units equipped with structured corrugated sheet packings. The HA approach is an alternative way to describe hydrodynamics and transport phenomena in processes, in which exact location of the phase boundaries is hardly possible. Contrary to the traditional models based on the film theory, separation columns can be described without using mass transfer coefficient correlations.

In this work, the HA approach was applied to carbon dioxide absorption into aqueous monoethanolamine. The composition profiles were determined in an absorption column filled with structured packings. For the model validation, experimental data from literature were used.

1. Introduction

The removal of carbon dioxide (CO₂) from gas mixtures is an important operation in many industrial processes, e.g. natural gas purification or oil refining. In many cases, the removal of CO₂ is realized by chemical absorption into aqueous MEA solution. The separation is usually performed in absorption columns filled with structured packings and operated counter-currently.

Adequate description of chemical absorption usually requires rigorous modelling methods. The rate-based approach represents a well-known way to design such columns (Kenig and Seferlis, 2009). It implies a direct consideration of actual rates of multicomponent mass and heat transfer as well as of chemical reactions within a column. The process hydrodynamics can be directly involved via correlations for hold-up, pressure drop, interfacial area and mass transfer coefficients. However, such correlations have to be obtained from expensive experimental investigations.

This dependency can be significantly reduced using the method of hydrodynamic analogy (HA) suggested by Kenig (1997). The HA method is based on a replacement of the actual complex process hydrodynamics by a combination of geometrically simpler flow patterns. Such a simplification has to be done in agreement with experimental observations of fluid flow in separation columns. Once the observed complex flow is represented by a combination of simplified flow patterns, the partial differential equations governing momentum, energy and mass conservation are applied to describe flow and transport phenomena in an entire separation unit (Shilkin and Kenig, 2005). Therefore, experimental determination of mass transfer coefficients is not required. The HA approach has been validated for different distillation processes (Shilkin et al., 2006) as well as for a reactive stripping process (Brinkmann et al., 2010). The simulated concentration profiles showed a good agreement with the experimental data. Furthermore, this method has also been applied to some reactive absorption systems (Brinkmann et al., 2009).

The objective of this work is an extension of HA approach to the CO₂ absorption by aqueous MEA. The extended HA model is applied to carry out a numerical analysis towards improvement of packing efficiency. Basically, such a modelling approach can be used for the identification of most suitable packing type as well as its adjustment to the specific process conditions.

2. Modelling

The main concept of the HA model applied in this work were suggested by Shilkin and Kenig (2005). In the physical model (see Figure 1), the packing is represented as a bundle of parallel inclined channels with identical cross section. The number of the channels as well as their diameter is determined from the packing surface area and corrugation geometry. The gas flow behaviour depends on the operating conditions and varies from laminar to fully developed turbulent flow. The liquid flows counter-currently to the gas flow in form of laminar films over the inner surface of the channels. The ratio wetted channel numbers to total channel numbers is the same as the ratio of effective (wetted) area to surface area of the packing:

$$\frac{n_w}{n_t} = \frac{a_e}{a_t} \quad (1)$$

The channels are inclined at the gravity flow angle α . The large-scale mixing of the both phases caused by abrupt flow redirection and redistribution is approximated by the periodic ideal mixing. Length of the undisturbed liquid flow z_L is set to be equal to the distance between the two neighbouring corrugation ridges, whereas for the gas flow, z_G is calculated as an average length of all channels in a packing layer. The model is adapted to isothermal conditions, which appear to be adequate for the example considered.

2.1 Mathematical Model

The liquid flow is described by the system of Navier-Stokes equations in the film-flow approximation (Shilkin et al., 2006):

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \mu_L \frac{\partial u_L(r)}{\partial r} \right) - \frac{\partial P_L}{\partial x} + \rho_L g \sin \alpha = 0, \quad \frac{\partial P_L}{\partial r} = 0. \quad (2)$$

For the description of the gas phase, the Boussinesq approximation is adopted:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \tilde{\mu}_G \frac{\partial u_G(r)}{\partial r} \right) - \frac{\partial P_G}{\partial x} + \rho_G g \sin \alpha = 0, \quad \tilde{\mu}_G = \mu_{G,\text{lam}} + \mu_{G,\text{turb}}, \quad \frac{\partial P_G}{\partial r} = 0. \quad (3)$$

The boundary conditions (see Figure 2) are as follows:

- At the solid surface: no-slip condition

$$r = R_h; \quad u = 0 \quad (4)$$

- At the channel symmetry axis: symmetry condition

$$r = 0; \quad \frac{\partial u}{\partial r} = 0 \quad (5)$$

- At the gas liquid interface: velocity and normal shear stresses are coupled via the conjugate boundary conditions:

$$r = R_h - \delta; \quad u_L = u_G, \quad \mu_L \frac{\partial u_L}{\partial r} = \tilde{\mu}_G \frac{\partial u_G}{\partial r} \quad (6)$$

Eqs (2)-(3) and the boundary conditions, Eqs (4)-(6), are supplemented by the following flow conservation conditions:

$$q_L = -2\pi \int_{R_h - \delta}^{R_h} u_L(r) r dr \quad (7)$$

$$q_G = 2\pi \int_0^{R_h - \delta} u_G(r) r dr \quad (8)$$

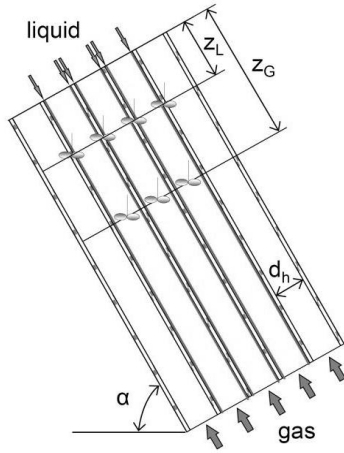


Figure 1: Physical model of structured packing (Shilkin et al., 2006)

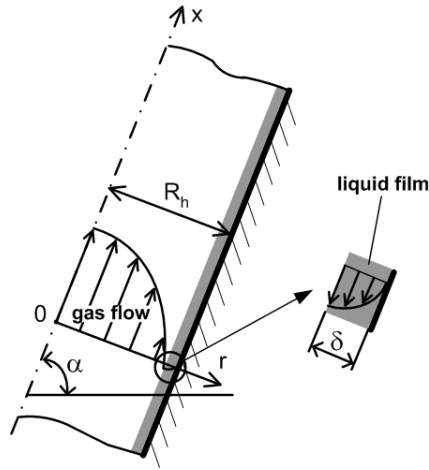


Figure 2: Schematic of the two-phase countercurrent flow in a channel (Shilkin et al., 2006)

The solution yields velocity profiles in both phases $u(r)$ together with the values of liquid film thickness $\delta(x)$ along the channel height which are used for the description of mass transfer.

2.2 Mass transfer

Mass transfer in each phase in a system comprising n components is described by the following transport equations:

$$u(r) \frac{\partial C_i}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \tilde{D}_i \frac{\partial C_i}{\partial r} \right) + R_i(\tilde{C}_i), \quad \tilde{D}_i = D_{i,\text{lam}} + D_{i,\text{turb}}, \quad D_{i,\text{turb}} = \frac{\mu_{\text{turb}}}{\rho S c_{i,\text{turb}}}, \quad i = 1 \dots n \quad (9)$$

Boundary conditions are defined

- at the entrance

$$x = 0; \quad C_i = C_i^0, \quad i = 1 \dots n \quad (10)$$

- at the channel wall and symmetry axis

$$r = R_h, \quad r = 0; \quad \frac{\partial C_i}{\partial r} = 0, \quad i = 1 \dots n \quad (11)$$

- at the phase interface: concentrations and temperatures in both phases are linked via the conjugate boundary conditions (thermodynamic equilibrium, energy and mass flux continuity)

$$r = R_h - \delta; \quad C_{G,i} = K_i C_{L,i}, \quad D_{L,i} \frac{\partial C_{L,i}}{\partial r} = D_{G,i} \frac{\partial C_{G,i}}{\partial r}, \quad i = 1 \dots n \quad (12)$$

Numerical solution of the system of equations using the Tri-Diagonal Matrix Algorithm (Patankar, 1980) yields concentration fields in both phases. These values are further used to obtain the average temperature and concentration profiles along the packing.

2.3 Parameters of HA-model

The solution of the mathematical model requires preliminary determination of the HA model parameters. These parameters can be subdivided into two groups, namely, geometry-related parameters, depending purely on the structured packing geometry, and hydrodynamics-related parameters, related both to the packing geometry and fluid flow conditions.

The geometry-related parameters are channel height, channel diameter, inclination angle, lengths of undisturbed gas and liquid flow. The number of wetted channels as well as parameters governing gas-

phase turbulence are examples of hydrodynamics-related parameters. The specific surface area is calculated using the correlation of Tsai et al. (2011). At higher gas loads, intensive turbulence occurs in the gas phase. This effect is accounted for within the HA-model by the gas-phase turbulent viscosity - see Eq.(3). The latter represent an external parameter to be determined by additional modelling (Shilkin et al., 2006). In this work, it is estimated on the basis of CFD simulations of a representative small periodical packing element using STAR CCM+.

2.4 Chemical reactions

Correct description of the liquid-phase reaction mechanism and kinetics is important for the overall chemical absorption modelling, especially regarding the interfacial mass transfer. The reactions accompanying the absorption of CO₂ by aqueous MEA solutions are complex, their detailed description can be found in Kucka et al. (2003). According to Hikita et al. (1977), for the CO₂-MEA system, the carbamate formation is considered as the main reaction that can be formulated as



This reaction is treated as an irreversible second-order reaction, with the reaction rate

$$R = k_R [\text{CO}_2][\text{MEA}] \quad (15)$$

and reaction rate constant given by

$$\log(k_R) = 10.99 - \frac{2152}{T} \quad (16)$$

2.5 Physical properties

In most works dealing with the modelling of CO₂ absorption by aqueous MEA solution, the influence of the CO₂ concentration on the liquid-phase density and surface tension finds no consideration. The data are usually taken either from Cheng et al. (1996) or from Vázquez et al. (1997). However, in reality, the dependence on the CO₂ concentration in the solution is significant, and, hence, we used here correlations in which the CO₂ impact is taken into account. A summary of the physical properties and corresponding literature sources used in our work is given in Table 1.

Table 1: Summary of physical properties

| Parameter | Phase | Reference/ Comment |
|------------------------|--------|---|
| Density | Liquid | Han et al. (2012) |
| | Vapour | Reid et al. (1986) |
| Diffusion coefficients | Liquid | Versteeg and van Swaaij (1988), Snijder et al. (1993) |
| | Vapour | method of Fuller, Reid et al. (1986) |
| Viscosity | Liquid | Weiland et al. (1998) |
| | Vapour | method of Wilke, Reid et al. (1986) |
| Surface Tension | Liquid | Dong et al. (2012) |
| Henry coefficients | | Brettschneider et al. (2004), Austgen et al. (1989) |

3. Simulation results

For the validation of the HA model, experimental data were taken from the thesis of Notz (2009). He performed experiments for absorption of CO₂ by MEA in a pilot plant with 0.125 m inner diameter, filled with 4.2 m high Montz packing B1-250. For the gas phase, only concentrations at the column top and bottom were measured. For the liquid phase, full concentration profiles were determined.

The required parameter for the proper description of the gas-phase turbulence in the HA model was estimated using CFD analysis for a representative element of Montz B1-250. As a representative element, the criss-crossing suggested by Petre et al. (2003) is chosen.

For the numerical solution, the transport equation, Eq (9), is converted into a dimensionless form and further discretised. Due to the high reaction rate of the carbamate formation (Eq (14)), a fine grid near the gas-liquid interface is applied. The required number of grid points was estimated by a grid independence study.

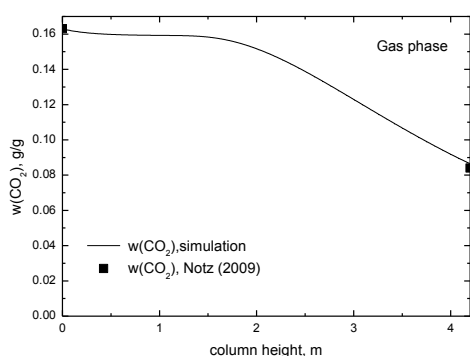


Figure 3: Gas phase simulations (HA) and literature data from Notz (2009)

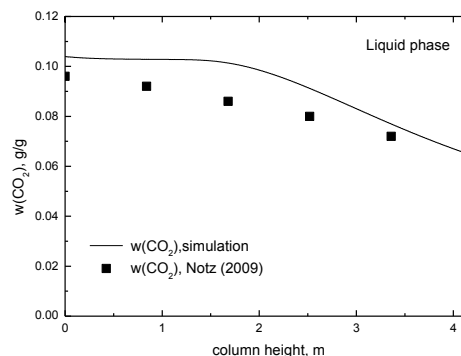


Figure 4: Liquid phase simulations (HA) and literature data from Notz (2009)

The model validation is based on the reference experiment No. 29 of Notz (2009), with an F-factor of $1.64 \text{ Pa}^{0.5}$ and a liquid load of $15.54 \text{ m}^3/(\text{m}^2\text{h})$ at the column bottom. The CO_2 loading in the liquid phase at the column top is $0.306 \text{ mol CO}_2 / \text{mol MEA}$. The simulated carbon dioxide mass fraction profiles and experimental data of Notz (2009) along the column height, starting from the bottom, are shown for the gas phase in Figure 3 and for the liquid phase in Figure 4. The simulated concentration profiles are in good agreement with the experimental data.

4. Conclusions

Accurate description of separation processes in columns filled with structured packings requires the use of rigorous models. The widely used rate-based modelling approach depends on mass transfer coefficients that have to be determined in extensive and expensive experimental studies. A novel modelling approach based on the application of hydrodynamic analogies suggests an alternative way to describe separation processes, which does not require the mass transfer coefficients.

In this work, the HA approach is applied to the description of a chemical absorption system in which CO_2 is absorbed by aqueous MEA solution. For the numerical solution of the transport equations, a fine grid in the area close to the gas/liquid interface is used. Most of the HA model parameters can be directly determined from the packing geometry, whereas the gas-phase turbulence is evaluated using additional CFD simulation of a representative packing element.

First model validation was performed against experimental data from the literature, and a fairly good agreement was found. This proves that the extended HA model is able to describe chemical absorption systems properly. In further investigations, the HA approach will be used for the identification of the most suitable packing type as well as for the packing adjustment to the CO_2/MEA system.

Notation

| | |
|-------|--|
| a_e | packing effective specific area, $\text{m}^2 \text{m}^{-3}$ |
| a_t | packing surface area, $\text{m}^2 \text{m}^{-3}$ |
| C | molar concentration of a component, mol m^{-3} |
| c_t | total molar concentration, mol m^{-3} |
| D | diffusivity, $\text{m}^2 \text{s}^{-1}$ |
| d_h | channel hydraulic diameter, m |
| g | gravity, m s^{-2} |
| K | distribution coefficient |
| k_R | second-order reaction rate constant, $\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$ |
| n_t | total number of channels |
| n_w | number of wetted channels |
| P | pressure, Pa |
| q | volumetric flow rate, $\text{m}^3 \text{s}^{-1}$ |
| R | reaction rate, $\text{mol m}^{-3} \text{s}^{-1}$ |
| R_h | channel hydraulic radius, m |
| r | radial coordinate, m |
| Sc | Schmidt number |

| | |
|-----|--|
| T | temperature, K |
| u | local velocity, m s^{-1} |
| x | axial coordinate, m |
| z | length of an undisturbed fluid flow, m |

Greek letters

| | |
|----------|-----------------------------|
| α | gravity flow angle |
| δ | film thickness, m |
| μ | dynamic viscosity, Pa s |
| ρ | density, kg m^{-3} |

Subscripts

| | |
|------|---------------|
| G | gas phase |
| i | component i |
| L | liquid phase |
| lam | laminar |
| turb | turbulent |

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