Porous media Eulerian computational fluid dynamics (CFD) model of amine absorber with structured-packing for CO2 removal

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HIGHLIGHTS

- A porous media CFD model was developed for amine absorber with structured-packing.
- Porous resistance, gas–liquid momentum exchange, and liquid dispersion were included.
- Mass transfer between two phases and chemical reaction in liquid phase were involved.
- Pressure drop, liquid holdup and CO2 concentration were obtained from the CFD model.

A R T I C L E  I N F O

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A B S T R A C T

A gas–liquid Eulerian porous media computational fluid dynamics (CFD) model was developed for an absorber to remove CO2 from natural gas by mono-ethanol-amine (MEA). The three dimensional geometry of the amine absorber packed with nine elements of Mellapak 500.X (M500X) was constructed for the CFD domain. The momentum conservation equation included the porous resistance, gas–liquid momentum exchange and liquid dispersion to replace the structured-packing by the porous media model. The mass conservation equation involved the mass transfer of CO2 gas into the MEA solution and one chemical reaction. The mesh independent test was performed on coarse, medium and fine meshes and the medium mesh (37,400 cells) was selected for further investigation. Parameters of the CFD model were adjusted to fit experimental data (wet pressure drop, liquid holdup, and CO2 mole fraction along the column height) measured in a CO2-MEA system on M500X. This study demonstrated that the porous media CFD model can treat both hydrodynamics and CO2 removal in the amine absorber with structured-packing.

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1. Introduction

Carbon dioxide (CO2) removal plays a crucial role in many industrial processing activities such as oil refining, the synthesis of ammonia, and natural gas purification (Aroonwilas et al., 2003). In these processes, CO2 and hydrogen sulfide (H2S) are considered to be impurities, and the acid gases must be reduced to prevent corrosion to materials and harmfulness to both the environment and human beings (Rahimpour et al., 2013).

CO2 is separated or captured by absorption, adsorption, membrane, and cryogenic technologies (Pires et al., 2011). The amine absorption technology is well-established with numerous industrial installations (Zhuang et al., 2011) and ready for large scale use (Kwak et al., 2012). Aqueous solutions of ethanolamine, especially monoethanolamine (MEA) and diethanolamine (DEA), are often used for the absorbent because of low volatility, thermal stability, high reactivity, and low cost (Hikita et al., 1977). The performance of the amine absorber is generally determined by mass-transfer efficiency of column packings providing the gas and liquid contacting area (Aroonwilas et al., 2001).

Structured packings are well recognized as column internal devices offering excellent mass transfer efficiency and low pressure drop (Aroonwilas et al., 2001; Beugre et al., 2011; Owens et al., 2013; Sun et al., 2013). The structured-packing has been widely accepted in many industrial applications to distillation, dehydration, extraction, and absorption due to a large effective area per unit volume ranging from 125 to 750 m2/m3 and a large void fraction (Aroonwilas et al., 2001; Haroun et al., 2014, 2012; Shilkin et al., 2006).

In recent years, many experimental and modeling approaches have been reported for amine absorbers with the structured-packings. The CO2 reaction kinetics with MEA and DEA were studied at various temperatures (Hikita et al., 1977). The vapor–liquid
equilibrium of amine-CO$_2$ systems was presented as a function of temperature and amine concentration (Penttilä et al., 2011).

The mass transfer efficiency of structured-packings was investigated in a MEA-CO$_2$ system according to operating and design parameters (Aroonwilas et al., 2001). A mechanistic model that was able to predict hydrodynamics and mass transfer performance was proposed, and its results were compared to experimental data for several structured-packings and operating conditions (Aroonwilas et al., 2003). A hydrodynamic analogy-based model (HAM) with a simplified internal packing geometry was presented to predict temperature and composition profiles in distillation columns (Shilkin et al., 2006). A two-dimensional tubular channel model was solved by the volume of fluid (VOF) method, and the liquid holdup and mass transfer were studied as a function of the liquid flow rate and structured packing geometry (Haroun et al., 2012).

The computational fluid dynamics (CFD) was a powerful tool to investigate effective interfacial area, liquid holdup, and fluid flow behaviors in structured packings (Haroun et al., 2014). The fluid dynamic performance of packing internals such as gas and liquid distributors, and liquid collectors was analyzed by using three-dimensional (3D) CFD simulation, compared to experimental measurements of the gas velocity at the top of a packed column (Mohamed Ali et al., 2003). A multi-scale CFD simulation sequentially approaching from small to large scales of a structured-packing column was presented to examine the liquid holdup and pressure drop (Raynal and Royon-Lebeaud, 2007). Another multi-scale strategy combining a small scale gas–liquid VOF model with a unit network model was proposed to calculate the liquid holdup and liquid distribution (Sun et al., 2013). The representative element unit (REU) or periodic element unit (PEU) corresponding to a few centimeters of packing was used to calculate the pressure drop and mass transfer by 3D CFD simulation (Lautenschleger et al., 2015; Raynal and Royon-Lebeaud, 2007; Sun et al., 2013).

Recently, Owens et al. (2013) solved gas phase hydrodynamics by a 3D turbulent CFD model, considering a real geometry of a corrugated and perforated structured-packing (about 50 cm height) with over 50 million meshes. The dry pressure drop was obtained directly from the CFD simulation and validated with experimental data. Fournari et al. (2013) addressed a gas–liquid porous media CFD model incorporated with the porous resistance, momentum transfer between the two phases, and liquid dispersion. The liquid spreading coefficient was estimated from experimental measurements. Since the porous media model simplified the complex structured-packing geometry to a homogeneous porous material, the mesh number was reduced much. The study showed that the porous media CFD model can reflect hydrodynamics and gas–liquid interactions of structured-packings. However, there remains a need for a complete porous media CFD model that can treat mass transfer and chemical reaction in the amine-CO$_2$ system.

In this study, the gas–liquid Eulerian porous media CFD model is extended to consider mass transfer and chemical reaction in the amine absorber with structured-packing. Model parameters of the porous resistance and momentum exchange are adjusted to fit experimental data (pressure drop and liquid holdup) measured on Mellapak 500X (M500X). The mass transfer rate coefficient is tuned with the aid of a CO$_2$ concentration profile experimentally measured by Aroonwilas et al. (2003). This study shows that the porous media CFD model can represent both hydrodynamics and mass transfer in the amine absorber with structured-packing for CO$_2$ removal.

In Section 2, the CFD calculation domain is described for an amine absorber packed with nine elements of M500X. Section 3 presents the porous media CFD model including porous resistance, momentum exchange, liquid dispersion, mass transfer and chemical reaction. Section 4 covers the mesh independent test, the model parameters adjustment, and the effect of mass transfer. Finally the conclusion is followed in Section 5.

### 2. Amine absorber for CO$_2$ removal

The dimension of an amine absorber was obtained from the literatures (Aroonwilas et al., 2003, 2001). The geometric characteristics (i.e., specific surface area, voidage, corrugation angle, and element height) of three Mellapak structured-packings are listed in Table 1. The corrugated structured-packing height was 2.205 m corresponding to the nine packings of M500X (Mellapak 500X). The voidage or porosity ($\varepsilon$) is defined as

$$
\varepsilon = \frac{V_C + V_L}{V} = \alpha_G + \alpha_L
$$

where $V_C$ and $V_L$ are the gas and liquid volumes, respectively, and $V$ is the total volume. The sum of the gas ($\alpha_G = V_C/V$) and liquid ($\alpha_L = V_L/V$) volume fractions is the voidage ($\varepsilon$). Fig. 1 illustrates that the representative elementary volume ($V$) includes $V_C$, $V_L$, as well as the solid volume of corrugated sheets. The transport equations will be expressed inside the elementary volume (see Section 3).

#### 2.1. Geometry of amine absorber and liquid distributor

The three dimensional (3D) geometry of the amine absorber is depicted in Fig. 2. The amine absorber consists of nine elements (element height of 24.5 cm), a liquid distributor in the top, and a bottom side for the uniform gas inlet. The diameter of the column is equal to that of the packing element (0.1 m). The liquid distributor with twelve holes of 1.2 cm diameter is located at 0.6 cm just above the packing. The front and top views are shown in Fig. 2b and c, respectively. The mono-ethanol-amine (MEA) solution is injected through the liquid distributor, and natural gas containing 15 mol% CO$_2$ enters from the bottom of the amine absorber.

Since the structured-packing was assumed as a porous medium in this study, the geometric characteristics of the packing were not fully considered. However, the porous media zone mimicked key features of the structured-packing by means of the porous resistance and liquid dispersion. The porous media model will be presented in Section 3.

#### 2.2. Meshing of CFD calculation domain

The mesh structure of the amine absorber is shown in Fig. 3. The top of the column has a fine hexahedral mesh structure to represent the twelve holes in the liquid distributor, while a relatively coarse mesh structure is used in the porous zone just below the distributor (see Fig. 3c and d). The non-conformal meshing strategy is applied to reduce the number of meshes at the interface between the liquid distributor and the porous zone.

Keeping the same number of meshes in the non-porous zone (top and bottom of the column), coarse, medium, and fine meshes (about 12,000, 37,000, and 103,000, respectively) are implemented to the porous zone in order to investigate the effect of the number of meshes (see Section 4.1).

<table>
<thead>
<tr>
<th>Packing</th>
<th>M250X</th>
<th>M500X</th>
<th>M500Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area, $a_s$ ($m^2/m^3$)</td>
<td>250</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Voidage (or porosity), $\varepsilon$ (-)</td>
<td>0.98</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>Corrugation angle, $\phi$ (°)</td>
<td>60</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>Element height, $h_e$ (m)</td>
<td>0.253</td>
<td>0.245</td>
<td>0.205</td>
</tr>
</tbody>
</table>
3. Porous media Eulerian CFD model

A 3D porous media CFD model was developed for the amine absorber. The fluid flow was assumed to be incompressible and isothermal. The gas and liquid phases were modeled by the Eulerian approach that treats the two phases flow as the inter-penetrating continua. The porous resistance and liquid dispersion were considered to imitate hydrodynamics of the structured-packing. The momentum and mass transfers between the two phases were taken into account and one chemical reaction
occurred in the liquid phase. The momentum and mass equations deal with quantities that are averaged over a representative elementary volume (V) (Fourati et al., 2013), as shown in Fig. 1b.

3.1. Continuity equation

The continuity equation for the gas and liquid phases is expressed as follows:
\[
\begin{align*}
\frac{\partial (\alpha G \rho_G \bar{u}_G)}{\partial t} &= -\bar{\nabla} \cdot (\alpha G \rho_G \bar{u}_G) - r_{GL} \\
\frac{\partial (\alpha L \rho_L \bar{u}_L)}{\partial t} &= -\bar{\nabla} \cdot (\alpha L \rho_L \bar{u}_L) + r_{GL}
\end{align*}
\]
where \( \rho \) is the density (kg/m\(^3\)), \( \bar{u} \) is the interstitial volume-averaged velocity vector, and \( r_{GL} \) (kg/m\(^3\)/s) is the total mass transfer rate per unit volume from gas to liquid. The subscripts \( G \) and \( L \) stand for gas and liquid. The gas and liquid volume fractions (\( \alpha_G \) and \( \alpha_L \)) change with time \( (t) \) and space \( (x, y, \text{and } z) \) that are the independent variables. The Nabla operator \( (\nabla) \) is a spatial derivative vector. The continuity equation means the overall mass balance in each phase. The first term of Eq. (2) is the accumulation term of the total mass within the unit volume. The second term denotes the convection term of the total mass.

3.2. Momentum conservation equation

The following assumptions and limitations should be recognized in the porous media momentum model (ANSYS, 2013): (1) the effect of turbulence is ignored in the porous medium, (2) the porosity \( (\varepsilon) \) of packing is isotropic, (3) the interstitial velocity is velocity with the porosity, and (4) the porous media momentum resistance is calculated separately in each phase.

The porous media model was constructed by adding momentum sources \( (S) \) into the conventional incompressible Newtonian fluid momentum equation (or Navier–Stokes equation).

\[
\rho \frac{\partial (\alpha_a \bar{u}_a)}{\partial t} = -\rho_a \bar{u}_a \cdot \nabla \left( \alpha_a \bar{u}_a \right) - \bar{\nabla} \cdot \left( \rho_a \bar{u}_a \bar{u}_a \right) + \rho_a \alpha_a \bar{g} - S_a
\]

where \( P \) is the pressure, \( \bar{g} \) is the gravitational acceleration, and \( \mu \) is the viscosity. The momentum source term \( (S) \) includes the porous resistance \( (\bar{F}_{\text{porous}}) \), the momentum exchange \( (\bar{F}_{\text{exch,gl}}) \), and the liquid dispersion \( (\bar{F}_{\text{disp,gl}}) \):

\[
\bar{S}_C = \frac{\alpha_G r_{\text{porous,G}}}{\varepsilon} + \varepsilon \bar{F}_{\text{exch,gl}} + \bar{F}_{\text{disp,G}}
\]

\[
\bar{S}_L = \frac{\alpha_L r_{\text{porous,L}}}{\varepsilon} - \varepsilon \bar{F}_{\text{exch,gl}} + \bar{F}_{\text{disp,L}}
\]

where \( \alpha_a/\varepsilon = V_L/(V_L + V_C) \) means the liquid volume fraction to the empty volume of packing (Fourati et al., 2013).

3.2.1. Porous resistance force

The porous resistances (or solid–fluid drag forces) were derived from a generalized Ergun correlation in packed-beds (Fourati et al., 2013; Iliuta et al., 2004):

\[
\bar{F}_{\text{porous,G}} = (1 - f_s) \left( \frac{a \cdot E_1}{35} \right) \left( \frac{\rho a^2 G}{\varepsilon} \left( \frac{1}{\varepsilon} \right) \left( \frac{1}{\bar{u}_G} \right) \right) \bar{u}_G
\]

\[
\bar{F}_{\text{porous,L}} = f_s \left( \frac{a \cdot E_2}{36} \right) \left( \frac{\rho a^2 L}{\varepsilon} \left( \frac{1}{\varepsilon} \right) \left( \frac{1}{\bar{u}_L} \right) \right) \bar{u}_L
\]

where \( E_1 \) and \( E_2 \) are the Ergun coefficients, \( a \) [m\(^2\)/m\(^3\)] is the specific surface area of the packing, and \( f_s \) is the fraction of wetting area. \( a \) and \( b \) are the modification factors for the Ergun coefficient. The wetting-area fraction \( (f_s) \) is the ratio of the effective contacting area \( (a_e) \) between the gas and liquid phases to the specific surface area \( (a) \), which plays a crucial role in connecting hydrodynamics and mass transfer. Since the effective interfacial area \( (a_e) \) cannot be directly captured because of an interpenetrating behavior of multiphase flow in the Eulerian approach, a function inspired from Tsai et al. (2011) is proposed:

\[
f_s = \frac{a_e}{a} = 1.34 \left( \frac{\rho a^{1/3}}{\varepsilon} \right)^{4/3} \left( \frac{Q}{\varepsilon^2} \right)^{0.116} Q = 5.1189A_h^{2.854}
\]
where \( \sigma \) [N/m] is the surface tension of MEA solution, \( Q \) [m\(^3\)/s] is the liquid flow rate, \( L_p \) [m] means the wetted perimeter, \( A \) [m\(^2\)] is the cross-sectional area of column, and \( h_l \) is the liquid holdup. The second equation of Eq. (6) was regressed from air–water experimental data (Suess and Spiegel, 1992) for liquid holdup (\( h_l \)) versus liquid load (\( q_l \)) in M500X (see Section 4.3 for the experimental data). When the physical properties (\( \rho_l \), \( \alpha_l \), and \( L_p \)) are assumed to be constant, \( f_e \) is expressed as a function of \( h_l \) and has an average value of 0.75 (or \( \alpha_l = 375 \) m\(^2\)/m\(^3\)) at a mean liquid holdup of \( h_l = 0.094 \) (see Section 4.2). The effective surface area (\( A_g \)) for mass transfer changes dynamically within the porous media domain according to the local liquid holdup (\( h_l \)) calculated from the Eulerian CFD model. It is expected that Eq. (6) is valid in the range of 0.05 \( \leq h_l \leq 0.15 \).

The first and second terms on the right hand side in Eq. (5) represent the viscous and inertial loss of momentum, respectively. In general, the solid–fluid drag forces are described as the following forms (ANSYS, 2013):

\[
\vec{F}_{\text{porus}} = \mu \vec{R}_{\text{vis}} \cdot \vec{u} + \frac{1}{2} \rho_i \left| \vec{u} \right| \vec{R}_{\text{in}} \cdot \vec{u}
\]

(7)

Thus, the viscous and inertial loss resistances (\( R_{\text{vis}} \) and \( R_{\text{in}} \)) are given in the analogy of Eqs. (5) and (7):

\[
R_{\text{vis},G} = (1-f_e) \frac{a \cdot E_1}{36} \quad R_{\text{in},G} = (1-f_e) \frac{b \cdot E_2}{3} \quad a_i \alpha_l \quad \frac{1}{\rho_i} \quad \vec{u}
\]

(8)

The gas–solid (\( K_{\text{GS}} \)) and liquid–solid (\( K_{\text{LS}} \)) coefficients are rearranged from Eq. (5) for further usage.

\[
K_{\text{GS}} = \frac{a \cdot E_1}{36} \left( \alpha_G \frac{b \cdot E_2}{6} + \frac{\alpha_l \alpha_r \rho_C}{\alpha_r} \right) \quad \vec{u}
\]

(9)

\[
K_{\text{LS}} = \frac{a \cdot E_1}{36} \left( \alpha_L \frac{b \cdot E_2}{6} + \frac{\alpha_l \alpha_r \rho_C}{\alpha_r} \right) \quad \vec{u}
\]

(10)

3.2.2. Gas–liquid momentum exchange

The gas–liquid momentum exchange (\( \vec{F}_{\text{exch,GL}} \)) may be written as follows (Fourati et al., 2013):°

\[
\vec{F}_{\text{exch,GL}} = f_e \frac{c \cdot E_1}{36} \left( \alpha_G \frac{d \cdot E_2}{6} + \frac{\alpha_l \alpha_r \rho_C}{\alpha_r} \right) \cdot \left( \vec{u} \cdot \vec{c} - \vec{u} \cdot \vec{l} \right)
\]

\[
= K_{\text{CL}} \left( \vec{u} \cdot \vec{c} - \vec{u} \cdot \vec{l} \right)
\]

(10)

where \( c \) and \( d \) are the modification factors for the Ergun coefficients. The two parameters should be adjusted according to the type of structured-packings. \( K_{\text{CL}} \) is the drag coefficient of momentum exchange.

3.2.3. Liquid dispersion force

The radial dispersion force model for structured-packing was originated from the mechanical dispersion in a trickle-bed reactor (Fourati et al., 2013; Lappalainen et al., 2009). In this work, the original model by Lappalainen et al. (2009) was used to consider the liquid dispersion phenomena in the amine absorption column. The gas and liquid dispersion forces (\( \vec{F}_{\text{disp}} \)) are defined as:

\[
\vec{F}_{\text{disp,G}} = a_G K_{\text{CG}} \vec{u}_{\text{D,G}} + \epsilon K_{\text{IC}} \left( \vec{u}_{\text{D,G}} - \vec{u} \right)
\]

\[
\vec{F}_{\text{disp,L}} = a_L K_{\text{CL}} \vec{u}_{\text{D,L}} - \epsilon K_{\text{IC}} \left( \vec{u}_{\text{D,L}} - \vec{u} \right)
\]

(11)

where the drag coefficients (\( K_{\text{CG}}, K_{\text{CL}}, \) and \( K_{\text{IC}} \)) are found in Eqs. (9) and (10). \( u_D \) is the drift velocity given by:

\[
\vec{u}_{\text{D,G}} = -f_{\text{spread}} \frac{\left| \vec{u}_C/a_G \right|}{a_G} \vec{v}_G
\]

\[
\vec{u}_{\text{D,L}} = -f_{\text{spread}} \frac{\left| \vec{u}_L/a_l \right|}{a_l} \vec{v}_l
\]

(12)

where \( f_{\text{spread}} \) is the spread factor whose dimension is the length. Here, it is evident that \( v_C = -v_l \) from Eq. (1). Note that the magnitude of the gas dispersion force (\( \vec{F}_{\text{disp,G}} \)) is much smaller than that of the liquid dispersion force (\( \vec{F}_{\text{disp,L}} \)). The spread factor was obtained from the liquid flow distribution interpreted with a convection–diffusion equation of \( q_l \) (liquid load or liquid volumetric flux, m\(^3\)/m\(^2\)/h) (Fourati et al., 2013):

\[
\frac{\partial q_l}{\partial t} = f \frac{d}{d \alpha} \left( \frac{\partial q_l}{\partial \alpha} \right)
\]

(13)

where \( q_l \) is the radial liquid load. A good spreading factor was found to be \( f_{\text{spread}} = 7.4 \) mm for M500X (Fourati et al., 2013). In the present simulation, this value was also used for M500X because of the same corrugated angle (60°).

The viscous and inertial momentum losses in porous media (\( \vec{F}_{\text{exch,GL}} \)), momentum exchange drag force (\( \vec{F}_{\text{exch,GL}} \)), and mechanical dispersion force (\( \vec{F}_{\text{disp,L}} \)) were supplied as the user defined function (UDF).

3.3. Species transport equation

It was assumed that there are two species such as CH\(_4\) and CO\(_2\) in the gas phase. It was also supposed that MEA and other species in the liquid phase do not vaporize into the gas phase. Even though the reactions during the absorption of CO\(_2\) into the aqueous amine solution are remarkably complex, just one chemical reaction is considered in this study for the CO\(_2\)-MEA system. Assuming that mass transfer between the gas and liquid phases occurs for only CO\(_2\), the mass conservation equation is expressed in the two phases.

\[
\frac{\partial (\alpha_i q_{l,i})}{\partial t} = -\vec{u}_l \cdot \nabla \left( \alpha_i q_{l,i} \right) + D_{l,i} \nabla^2 (\alpha_i q_{l,i}) - r_{GL,i}, \quad i = CO_2
\]

(14)

where \( D_i \) is the diffusion coefficient of species \( i \), \( r_{GL} \) is the mass transfer rate between gas and liquid applied only to CO\(_2\), and \( R_k \) is the homogeneous chemical reaction rate which will be described in detail in Section 3.3.2. Owing to the continuity equation, the mass conservation equation is given for (\( N-1 \)) species where \( N \) is the number of species.

3.3.1. Mass transfer rate (\( r_{GL} \))

In general, the overall mass transfer coefficient derived from the two film theory is used (Gabrielsen et al., 2006; McCabe et al., 2005):

\[
\frac{1}{K_s} = \frac{1}{K_G} + \frac{1}{H_k}
\]

(15)

where \( k_G \) and \( K_s \) are the mass transfer coefficients in the liquid and gas films, respectively, \( K_s \) is the overall liquid mass transfer coefficient, \( E \) stands for the enhancement factor promoted by chemical reaction, and \( H \) is the Henry's constant. Most of the overall mass transfer resistance (\( 1/K_s \)) comes from the liquid-side resistance (\( 1/K_s \)) in the CO\(_2\)-amine system (Hamborg and Vers-teeg, 2012; Tunnat et al., 2014). Thus, the overall mass transfer
coefficient may be assumed to:

$$K_x \approx E k_x$$  \hspace{2cm} (16)

The enhancement factor ($E$) was expressed as a function of the MEA concentration (Gabrielsen et al., 2006; Tobiesen et al., 2007). If the MEA concentration does not change much throughout the reaction zone, the factor can be treated as a constant. In fact, the MEA concentration varied from 2.6 to 3.0 kmol/m$^3$ in this amine absorber with the nine packs. A simple mass transfer rate for CO$_2$ with only the liquid film resistance is applied in this study:

$$r_{GL} = k_d a (P_{L,CO_2} - P_{CO_2})$$  \hspace{2cm} (17)

where $P_{L,CO_2}$ is the equilibrium liquid mass concentration of CO$_2$ at the gas–liquid interface. $k_d$ is a lumped value including the liquid film resistance and the enhancement by the chemical reaction, which depends on the system and can be estimated from theoretical or empirical correlations (Aroonwilas et al., 2003). The $P_{L,CO_2}$ is determined by Henry’s law:

$$P_{L,CO_2}^* = M_wCO_2 \frac{P_{CO_2}}{H_{CO_2-MEA}}$$  \hspace{2cm} (18)

where $M_wCO_2$ is the molecular weight of CO$_2$, $P_{CO_2}$[Pa] is the partial pressure of CO$_2$ in the gas phase, and $H_{CO_2-MEA}$ is the Henry’s constant of CO$_2$ in the aqueous MEA solution. The Henry’s constant for the MEA–CO$_2$ aqueous system was obtained from the vapor–liquid equilibrium in N$_2$O–CO$_2$ analogy (Clarke, 1964; Penttilä et al., 2011).

$$H_{CO_2-MEA} = H_{N_2O-MEA} \frac{H_{CO_2-water}}{H_{N_2O-water}}$$  \hspace{2cm} (19)

The Henry’s constants of CO$_2$ and N$_2$O in pure water ($H_{CO_2-water}$ and $H_{N_2O-water}$) as a function of temperature was found elsewhere (Penttilä et al., 2011). To obtain $H_{N_2O-MEA}$ at a liquid mole fraction of MEA ($x_{MEA}$) of 0.06 (or 31.7 wt%), a regression equation estimated from experimental data of Penttilä et al. (2011) is shown in Fig. 4. The Henry’s constant used in this study was $H_{CO_2-MEA}$=3690 Pa m$^3$/mol at 304 K.

### 3.3.2. Chemical reaction rate ($R$)

For the CO$_2$–MEA system, the reaction rate may be expressed by the 2nd-order kinetics (Hikita et al., 1977):

$$\text{CO}_2(l) + 2\text{HORNH}_2^+ + \text{HORNHCOO}^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{MEA} + \text{MEA}^+$$

$$R_{CO_2} = \frac{d}{dt} [L,CO_2] = -k_d [L,CO_2] [L,MEA]$$

$$k_d = k_0 e^{-E_a/(RT)}$$  \hspace{2cm} (20)

where $k_d$ is the chemical reaction rate constant depending on $T$.

which is expressed as an Arrhenius equation with the pre-exponential factor ($k_0$) and activation energy ($E_a$). Five species exist in the liquid phase: MEA, H$_2$O, HORNH$_2^+$, HORNHCOO$^-$, and CO$_2$(l). Since the molar concentration ($C_i = n_i/L_m$) is preferred rather than the mass concentration ($\rho_{L,i}$), the chemical reaction rate in Eq. (20) is converted into:

$$R_{CO_2} = \frac{dC_{CO_2}}{dt} = -k_d C_{CO_2} C_{MEA}$$  \hspace{2cm} (21)

The mass transfer rate ($r_{GL}$) and chemical reaction rate ($R_{CO_2}$) were also incorporated into the species transport equation by an UDF. After the MEA–CO$_2$ reaction, the physical properties of liquid (diffusivity, viscosity and surface tension) will change, and they may affect the effective interfacial area and the mass transfer coefficient. However, the effects were ignored in this simple reaction model.

### 3.4. Solution strategy and model parameters

The continuity equation, momentum and mass conservation equations were solved by using ANSYS Fluent (ANSYS Inc., USA). The phase coupled SIMPLE method was chosen for pressure–velocity coupling. The second–order upwind and QUICK schemes were used for the spatial discretization of the momentum and mass equations, and the volume fraction, respectively.

Table 2 shows parameter values of the porous media model which were used for the additional source term in the momentum equation. The Ergun coefficients ($E_1$ and $E_2$) reported for M250X by Iliuta and Larachi (2004) were taken without modification. However, as M500X was a packing material in this study, the four modification factors of Ergun coefficients ($a$, $b$, $c$, and $d$) were applied in Eqs. (8) and (10) and adjusted for M500X (see Section 4.3). The liquid spread factor ($f_{spread}$) proposed by Fourati et al. (2013) was taken. The wetted perimeter ($L_w$) was 4.05 m for M500X.

The model parameters related to mass transfer and chemical reaction are reported in Table 3. The liquid mass transfer coefficient ($k_d$) was initially guessed from Aroonwilas et al. (2003) and tuned with experimental data (see Section 4.3). The amine absorber was operated at $T$=304 K, and $P$=1 atm. The reaction rate coefficients ($k_0$ and $E_a$) were obtained from Hikita et al. (1977).

Table 4 presents the boundary conditions and the simulation parameters. The three mesh numbers of the porous media zone were tested to investigate the effect of the mesh number on the CFD solution. The multiphase Eulerian model was calculated by the unsteady-state, sequential (or pressure-based segregated), and implicit solver. Gas and liquid inlet boundary conditions (inlet BC) were taken from experimental conditions of Aroonwilas et al. (2003). The outlet boundary condition (outlet BC) of gas was set to the mass flow outlet, while that of liquid was the pressure outlet. The maximum iteration number was 100 at each time step and the convergence tolerance was $1 \times 10^{-3}$.

At the beginning of the simulation, gas and liquid were injected into the packed column which was initially empty. After a wetting
period of about 35 s, the mass transfer and chemical reaction started and it took about 15 s to reach a stable state. Thus, the operating time about 50 s was required to obtain a stable solution.

4. CFD simulation results

The gas–liquid Eulerian porous media CFD model was first of all solved on the three different mesh numbers. Then, liquid dispersion was examined along the height of the porous medium column. The CFD model parameters were adjusted with experimental data such as the wet pressure drop, liquid holdup, and CO2 concentration profile along the column height. Finally, the effect of mass transfer and chemical reaction was discussed.

4.1. Mesh independent test

A high-resolution mesh having 36,480 hexahedral cells was built in the non-porous zone (top and bottom of the column) because of the inlet and outlet of gas and liquid. The mesh structure of the non-porous zone was fixed. The mesh independent test was performed for only the porous zone.

The coarse (11,880 hexahedral cells), medium (37,440 hexahedral cells) and fine (103,455 hexahedral cells) meshes were built in the porous zone. The effect of the mesh number was examined on the total dry pressure drop, and gauge pressure, CO2 mole fraction and liquid holdup along the column height, as shown in Fig. 5. The liquid holdup \( h_L \) is a liquid volume fraction \( \langle \alpha_L \rangle \) averaged over an interesting volume:

\[
 h_L = \frac{\sum_i \alpha_L \Delta V_i}{\sum_i \Delta V_i} \tag{22}
\]

where \( \Delta V \) is the cell volume in the computational domain. Since the structured packing was regarded as a homogeneous porous material with viscous and inertial momentum loss, the effect of the mesh number was not significant on the total dry pressure drop, gauge pressure and CO2 concentration profile. The ratio of the total dry pressure drop \( \frac{\Delta P_{dry}}{P_{dry}} = 10.19 \text{ Pa} \) on the coarse grid to \( \frac{\Delta P_{dry}}{P_{dry}} = 10.43 \text{ Pa} \) on the fine grid is only 0.986, as seen in Fig. 5a. In Fig. 5b and c, it is more clear that the mesh number barely affect the gauge pressure \( P_{gauge} \) and CO2 mole fraction \( \langle Y_{CO2} \rangle \).

However, some discrepancy of the liquid holdup \( h_L \) is observed in Fig. 5d according to the mesh resolution. The liquid holdup of the coarse mesh shows a substantial difference from those of the medium and fine meshes. Since the accuracy of the CFD solution comes in general at the cost of computational time on the fine mesh, the medium mesh was selected for further researches.

4.2. Liquid dispersion and liquid holdup

Fig. 6 displays the liquid dispersion with time at the top of the column. Due to the dispersion force in Eqs. (11) and (12) with \( f_{spread} = 7.4 \text{ mm} \), the amine solution spreads out radially and fills up the column.

The liquid holdup of the whole column is shown in Fig. 7. The radially-averaged liquid holdup is a little smaller at both the top and the bottom than in the middle (see Fig. 7b), because a certain length from the distributor is necessary for even liquid spreading, and the gas upstream at the bottom slightly reduces the liquid holdup.

It is worth noting that the present porous media model cannot capture gas and liquid turbulences, boundary surfaces between the gas and liquid phases, and directional hydrodynamics appearing in the real structured packing. Thus, this model is suitable to identify an overall column performance rather than rigorous hydrodynamics inside the structured packing that are available in a detailed CFD model with the real geometry of packing.

4.3. Parameter adjustment of porous media CFD model.

The parameters of the porous media CFD model were adjusted with the experimental data measured in an amine absorber packed with M500X. Fig. 8 shows the wet pressure drop per unit length \( \frac{\Delta P_{wet}}{L}, \text{ Pa/m} \) versus the \( F \)-factor (gas load factor) defined as:

\[
 F - \text{ factor } = \frac{\dot{u}_G \sqrt{\rho_G}}{} \tag{23}
\]

where \( \dot{u}_G \) is the superficial gas velocity. The three experimental data measured in M500Y, M500X and M250Y at \( q_L = 24.4 \text{ m}^3/\text{m}^2/\text{h} \) were obtained from elsewhere (Sulzer, 2013; Tsai et al., 2011). The modification factors \( (a \text{ and } b) \) of Ergun coefficient in Eq. (8) were slightly changed to fit the packing, M500X (see Table 2). The CFD simulation results with the model parameters tuned for M500X agree well with its experimental data.

In Fig. 9, the liquid holdup obtained from the CFD simulation is compared to experimental data of M500Y from Suess and Spiegel (1992). It was indicated that M500X and M500Y had the same liquid holdup (Spiegel and Duss, 2014). The water liquid load \( (q_L) \) varies from 5 to 75 \( \text{m}^3/\text{m}^2/\text{h} \), and the \( F \)-factor is fixed at 0.21 \text{ Pa}^{0.5} \) (or \( q_G = 38.5 \text{ kmol/m}^2/\text{h} \)). The liquid holdup was averaged over the

Table 3

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid mass-transfer coefficient (m/s)</td>
<td>( k_i = 0.00104 )</td>
</tr>
<tr>
<td>Operating pressure (atm)</td>
<td>( P = 1.0 )</td>
</tr>
<tr>
<td>Operating temperature (K)</td>
<td>( T = 304 )</td>
</tr>
<tr>
<td>Pre-exponential factor (m^3/kmol/s)</td>
<td>( k_0 = 5.928 \times 10^4 )</td>
</tr>
<tr>
<td>Activation energy (cal/gmol)</td>
<td>( E_a = 4.274 \times 10^7 )</td>
</tr>
<tr>
<td>Diffusivities of gas and liquid (m^2/s)</td>
<td>( D_G = 2.8 \times 10^{-7}, D_L = 2.88 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh number ( N_{cell} )</td>
<td>About 12,000, 37,000, and 103,000 cells</td>
</tr>
<tr>
<td>Eulerian multiphase model</td>
<td>Un-steady-state, sequential, and implicit solver</td>
</tr>
<tr>
<td>Bottom-side BC</td>
<td>Incompressible ideal gas inlet (back flow), liquid (pressure-outlet), gas load (natural gas) = 38.5 kmol/m^2/h, and gas mole composition: ( CH_4 = 0.85, CO_2 = 0.15 )</td>
</tr>
<tr>
<td>Top-side BC</td>
<td>Gas (mass flow outlet)</td>
</tr>
<tr>
<td>Liquid distributor BC</td>
<td>Liquid (mass flow inlet), liquid load = 22.9 m^3/m^2/h, and liquid mass composition: MEA = 0.317, H_2O = 0.683</td>
</tr>
<tr>
<td>Maximum number of iterations</td>
<td>100</td>
</tr>
<tr>
<td>Convergence tolerance</td>
<td>( 1 \times 10^{-3} )</td>
</tr>
<tr>
<td>Total operation time (s)</td>
<td>50</td>
</tr>
</tbody>
</table>
whole packing zone. The liquid holdup increases with the increase of the liquid load. The modification factors (c and d) of the Ergun coefficient in Eq. (10) were adjusted to fit the experimental data (Suess and Spiegel, 1992).

The validation of the CFD model for the M500X packing itself was performed, adjusting the Ergun modification factors (a, b, c, d). The other parameters such as $f_{\text{spread}}$, $f_e$ (or $a_e$), $k_g$, $E_a$, and $H_{\text{CO}_2/\text{MEA}}$ were taken from the existing references without modification or with a simple regression. The mass transfer ($r_{\text{GL}}$) and chemical reaction ($R_{\text{CO}_2}$) rates in Eqs. (17) and (20) were applied to calculate the overall CO$_2$ removal efficiency on M500X. In Fig. 10a, the contour of the CO$_2$ mole fraction ($y_{\text{CO}_2}$) is shown for the whole packing zone.
column. The radially-averaged mole fraction along the height is compared to experimental data in Fig. 10b. Only the liquid mass transfer coefficient (\(k_0\)) was tuned to fit the experimental data carried out at \(q_G = 38.5 \text{ kmol/m}^2\text{h}\) and \(q_L = 22.9 \text{ m}^3\text{m}^2\text{h}\) (Aroonwilas et al., 2003). The adjusted \(k_0\) was 0.00104 m/s.

4.4. Effect of mass transfer and chemical reaction

The effect of the mass transfer coefficient (\(k_0\)) on the CO\(_2\) removal efficiency is shown in Fig. 11. The mass transfer coefficient was perturbed at 0.00104 ± 0.0002 m/s. The higher mass transfer coefficient leads to the higher CO\(_2\) removal, as expected.
A mass transfer and chemical reaction model reduced from Eq. (14) without hydrodynamics was taken into account for the comparison with the CFD model. Let the reduced model under the assumption of a homogeneous contact between the gas and liquid phases (i.e., $a_e = 390 \text{ m}^2/\text{m}^3$ or $f_e = 0.78$):

$$\frac{\partial}{\partial t}(\rho G_i) = -r_{Gi}, \quad i = \text{CO}_2$$

$$\frac{\partial}{\partial t}(\rho L_k) = +r_{Gi} + R_k, \quad k = \text{MEA, CO}_2$$

The three ordinary differential equations were solved by a time integrator for $11.3 \text{ s}$ which is required to pass through M500X ($h = 2.205 \text{ m}$) at the same gas flow rate as that of the CFD simulation, $q_G = 38.5 \text{ kmol/m}^2/\text{h}$.

When the mass transfer coefficient ($k'_x$) and chemical reaction rate constant ($k_c$) are the same as those of the CFD simulation, the result of the reduced model is compared with the experimental data and the CFD result of this study in Fig. 12. The height ($h$) of the experimental data was converted to the time ($t$) by the gas velocity ($u_G = 0.194 \text{ m/s}$). The reduced model with $k'_x = 0.00104 \text{ m/s}$ and $a_e = 390 \text{ m}^2/\text{m}^3$ shows a lower CO$_2$ removal efficiency than that of the CFD result. The difference results from $a_e$ and the liquid velocity ($u_L$). The $a_e$ varies along the column and $u_L$ is about $0.068 \text{ m/s}$ in the CFD model, while $u_L$ is regarded as the same velocity as $u_G$ in the reduced model. Since the slow liquid flow increases the absorption residence time, the CO$_2$ removal efficiency of the CFD model is higher.

Owens et al. (2013) who fully considered the detailed structure of a structured-packing (Mellapak N250Y, inner diameter of 14.6 cm and height of 47.5 cm) used 50 million meshes to calculate dry pressure drops of nitrogen gas by a turbulent CFD model. The rigorous CFD model may predict the wet pressure drop and liquid holdup without parameter tuning necessary in the porous media CFD model (see Table 2) at the expense of computational time. Furthermore, the effective specific area ($a_e$) would be computed directly by the rigorous CFD model. The porous media CFD model using about 3000 times smaller meshes than the rigorous one
The number of meshes affected little pressure drop and CO2 removal efficiency of the amine absorber was computed efficiently by the porous media model on the much reduced mesh.

5. Conclusions

The three dimensional geometry of an amine absorber packed with nine elements of Mellapak 500.X (M500X) was constructed for the porous media CFD simulation. The amine absorber was operated to remove 15 mol% CO2 contained in natural gas by using MEA (mono-ethanol-amine) as an absorbent. To represent the structured-packing by the porous media CFD model, the porous resistance force, the gas–liquid momentum exchange, and the liquid dispersion force were added into a typical momentum conservation equation. The mass conservation equation included the mass transfer between the gas and liquid phases, and one chemical reaction in the liquid phase. The two phases were modeled as a continuum by using the Eulerian approach. The three additional momentum forces, mass transfer and chemical reaction were supplied by user-defined functions. The gas–liquid Eulerian porous media CFD model was calculated by a finite volume-based solver, ANSYS Fluent.

The coarse (11,800 cells), medium (37,400 cells) and fine (103,400 cells) meshes were built for the mesh independent test. The number of meshes affected little the pressure drop and CO2 removal efficiency. However, the liquid holdup of the coarse mesh showed a significant difference from those of the medium and fine meshes. The medium mesh was selected among the three meshes as a compromise of accuracy and computational cost. The porous media momentum equation including the liquid dispersion force reflected the characteristics of radial liquid dispersion of structured-packing well. This study demonstrated that the porous media CFD model can predict the wet pressure drop, liquid holdup, and CO2 removal efficiency in the amine absorber, adjusting the modification factors of the Ergun coefficients (a, b, c, and d), and mass transfer coefficient ($K_g^*$).

In this study, the isotropic coefficients ignoring the directional property of structured-packing were used for the porous resistance, momentum exchange and liquid dispersion. An anisotropic approach could reflect the complex structure of corrugated and perforated sheets. It would be better to use a mass transfer coefficient dependent on the chemical reaction. More rigorous chemical reactions in the liquid phase must be considered in the future. The porous media CFD model presented in this study may be applied for the development and design of the liquid distributor and collector. This paper provided a potential to predict the CO2 removal efficiency by using appropriate parameters of the porous media model for a given structured-packing.

### Nomenclatures

#### Latin letters

- $A$: cross-sectional area of column (m$^2$)
- $a$: modification factor of Ergun equation
- $a_c$: effective interfacial area (m$^2$/m$^3$)
- $a_s$: specific surface area of structured-packing (m$^2$/m$^3$)
- $b$: modification factor of Ergun equation
- $c$: modification factor of Ergun equation
- $C_i$: molar concentration of species $i$ in liquid phase (kmol/m$^3$)
- $d$: modification factor of Ergun equation
- $D$: diffusivity coefficient (m$^2$/s)
- $E_1$, $E_2$: Ergun coefficients
- $E_a$: activation energy (cal/gmol)
- $F_{disp}^*$: liquid dispersion force (N/m$^3$)
- $f_{ex}^*$: fraction of wetting area
- $F_{por}^*$: porous resistance force (N/m$^3$)
- $f_{spread}^*$: spread factor (m)
- $g$: gravitational acceleration (m/s$^2$)
- $h_e$: element height (m)
- $h_l$: liquid holdup (m$^3$/m$^3$)
- $H$: Henry’s constant (Pa m$^3$/mol)
- $k_0$: pre-exponential factor (m$^3$/kmol/s)
- $k_c$: chemical reaction rate coefficient (m$^3$/kmol/s)
- $K_{CS}^*$: gas–solid drag coefficient (kg/m$^3$/s)
- $K_{CG}^*$: momentum exchange coefficient at the gas–liquid interface (kg/m$^3$/s)
- $K_{LS}^*$: liquid–solid drag coefficient (kg/m$^3$/s)
- $k_s$: liquid-side mass transfer coefficient (m/s)
- $k'_s$: lumped mass transfer coefficient (m/s)
- $K_s$: overall liquid mass transfer coefficient (m/s)
- $k_y$: gas-side mass transfer coefficient (m/s)
- $L_p$: wetted perimeter (m)
- $M_w$: molecular weight (kg/kmol)
- $P$: pressure (atm)
- $Q$: liquid flow rate (m$^3$/s)
- $q_{CG}^*$: gas load (kmol/m$^3$/h)
- $q_{fl}$: liquid load (m$^3$/m$^2$/h)
- $r$: radial component in a cylindrical coordinate system (m)
- $r_{CL}$: mass transfer rate between gas and liquid (kg/m$^3$/s)
- $R_i$: chemical reaction rate of species $i$ (kg/m$^3$/s)
- $R_{in}$: inertial momentum loss (1/m)
- $R_{vis}$: viscous momentum loss (1/m$^2$)
- $S$: momentum source term (N/m$^3$)
- $t$: time (s)
- $T$: temperature (K)
- $u$: interstitial volume-average velocity (m/s)
- $u_{CS}^*$: superficial gas velocity (m/s)
- $V$: volume (m$^3$)
- $x_i$: liquid mole fraction of species $i$
- $y_i$: gas mole fraction of species $i$

#### Greek letters

- $\alpha_G$: volume fraction of gas phase
- $\alpha_L$: volume fraction of liquid phase
\(e\) packing void fraction (porosity)
\(\theta\) corrugation angle (deg.)
\(\sigma\) surface tension of MEA solution (N/m)
\(\mu\) viscosity (kg/m/s)
\(\rho\) mass concentration or density (kg/m\(^3\))

Subscripts

\(D\) drift
\(G\) gas phase
\(L\) liquid phase

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References

