Dynamic modeling of absorption/desorption closed-loop including periphery

Mike Bothe, Iman Hami Dindar, Nicole Lutters, Eugeny Y. Kenig*
Chair of Fluid Process Engineering, Paderborn University, Paderborn, Germany

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ABSTRACT
Reactive absorption is one of the most important separation processes used within the chemical industry to address the environmental protection challenges. In this process, undesirable gaseous components are captured by chemical reaction in a solvent and the loaded solvent is then regenerated in the desorption unit. Both process steps take place simultaneously and strongly interact resulting in a very complex process behavior. To ensure stable and safe process operation, even in presence of instabilities/malfunctions, understanding of the dynamic process behavior is essential. In this work, the development of a novel dynamic model for simulation of a reactive absorption/desorption process in a closed-loop configuration including the periphery of the plant is presented. The validation of the model is accomplished based on two dynamic experiments carried out in our own pilot plant. The deviations between experimental and simulated outlet gas concentrations are below 10% for both experiments.

1. Introduction
Absorption units are usually complemented by desorption columns to regenerate the solvent, thus building a closed-loop configuration. As column internals, various packings, both structured and random, are applied to ensure a large contact area between the gas and the solvent. Packed columns also contain liquid distributors that help to realize even distribution of the solvent. Furthermore, the periphery of the plant comprises several heat exchangers (HEs) and pipelines. Each of the plant components, as those shown in a typical configuration in Fig. 1, influences the overall process behavior. Unforeseen changes in the process or plant conditions can lead to hazardous situations. Examples of such situations are flooding of the columns, a large increase in pressure or an insufficient absorption of toxic gas components, which can be very dangerous. In order to avoid the hazardous situations, understanding of the dynamic process behavior is necessary.

Different groups studied dynamics of absorption processes using both modeling and experimental analysis. Kvamsdal et al. (2009) theoretically investigated the dynamic process behavior for a stand-alone absorption column using an equilibrium stage approach. They claimed that their model had been validated. However, this was done only for a steady-state process, with the experimental data from the MEA campaign carried out at the University of Texas at Austin, USA (Dugas, 2006). Ziaii et al. (2011) developed a dynamic rate-based model for a stand-alone desorption column. Due to the high temperatures in the column, the reactions were considered as instantaneous. Again, the dynamic model could not be validated due to lacking experimental data on transient process behavior. Gaspár and Cormos (2011) investigated the absorption/desorption closed-loop process using the rate-based approach. They considered the reaction kinetics only for the “main” reaction between MEA and CO₂, while the influence of further reactions encountered in the system was neglected. Biliyok et al. (2012) and Åkesson et al. (2012) took all reactions into account. However, the reactions were treated as instantaneous (in both the desorption and absorption column). Due to the lower temperatures in the absorption column, this assumption is questionable. None of the works cited above considered the influence of the periphery and non-separating column internals like liquid distributors on the process dynamics. Harun et al. (2012) included the reboiler and a HE in their closed-loop model. The absorption/desorption process in the columns was modeled with the rate-based approach using enhancement factors; in contrast, the HE was considered as an equilibrium stage. The influence of the liquid distributors or the pipelines on the process dynamics was neglected. During the last five years, publications have largely been focused on data-driven models governing transient absorption/desorption process behavior. However, the necessary data were generated with non-validated and mostly too simplified physical concepts (Wu et al., 2020).

* Corresponding author.
E-mail address: eugeny.kenig@upb.de (E.Y. Kenig).

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Few experimental studies on absorption dynamics were published, but all published data are incomplete. Faber et al. (2011) presented three different experiments on the dynamic closed-loop process behavior, without giving sufficient details on the geometry and periphery. For instance, no information is available for the liquid distributors and the periphery. For instance, no information is available for the liquid distributors (Bothe et al., 2021). Since non-separating column internals on the overall process dynamics, studies have shown a significant influence of the periphery and the liquid distributors and the periphery is still missing in this paper. Thus, any validation of a dynamic closed-loop model with experimental data is missing.

In this paper, a novel model for the dynamic simulation of the overall closed-loop absorption process is presented. The model was developed and validated against experimental data. The packings installed in the absorption and desorption columns are modeled using the rate-based approach. Reaction kinetics, both in the film and the bulk region, and the influence of the electrolytes were taken into account, because approaches with lower model rigor fail to capture absorption process kinetics (Kenig et al., 2003). Furthermore, our preliminary simulation studies have shown a significant influence of the periphery and the non-separating column internals on the overall process dynamics, especially regarding the liquid distributors (Bothe et al., 2021).
information on the liquid distributors is neither available for the pilot plant built in Esbjerg, Denmark (Faber et al., 2011) nor for the Australian pilot plant (Bui et al., 2016), we carried out transient experiments at our own pilot plant (Fig. 1) and obtained the validation data for the simulations. This pilot plant has been basically designed as a multi-purpose set-up and experiments can be carried out in different configurations, e.g., with single packed columns or in the closed-loop mode. The latter mode was used in this work. A continuous measurement of liquid-phase and gas-phase compositions was, however, not possible because the plant was designed for investigations of steady-state absorption/desorption operations.

2. Dynamic modeling

The typical absorption plant, as shown in Fig. 1, consists of several components, all being important for dynamic modeling. For these components, different dynamic modeling approaches were used that are listed in Table 1. Their detailed description is given in the next sections.

2.1. Dynamic rate-based approach

Schneider et al. (1999) developed a rate-based dynamic model for the chemical absorption of coke oven gas (see Fig. 2). This model is adapted here for the description of the absorption/desorption processes within the columns internals. Each stage of the columns is described with the two-film theory. The resistance to mass transfer is concentrated in thin films adjacent to the phase interface and the mass transfer occurs within this film by steady-state molecular diffusion. The diffusion and reaction kinetics are directly accounted for in the mass and heat balance equations, while necessary parameters for calculation are determined with correlations obtained from the literature. Furthermore, the specific features of electrolyte solutions are included. In the following, the model equations are presented in a general form.

2.1.1. Bulk phases

For the liquid (solvent) bulk phase, the component material and energy balance equations are formulated as follows:

\[
\frac{\partial}{\partial t} \left( L_i^{lb} x_i^{lb} \right) = \frac{\partial}{\partial z} \left( L_i^{lb} x_i^{lb} \right) + \left( u_i^{lb} d_i + R_i^{lb} \phi_i^{lb} \right) A, \quad i = 1, \ldots, NCl
\]  

\[
\frac{\partial}{\partial t} \left( H_i^{lb} \right) = \frac{\partial}{\partial z} \left( H_i^{lb} \right) + q_i^{lf} A
\]

The volumetric liquid holdup \( \phi_i^{lb} \) depends on the gas and liquid flow rates and is determined from empirical packing correlations. In this work, the correlation of Billet and Schultes (1999) is used.

For the gas bulk phase, the balance equations looks similar, but the specific molar holdup \( U_g^{gb} \) is mostly neglected due to the low gas-phase density, and the component balance equation for the gas phase becomes:

\[
0 = \frac{\partial}{\partial z} \left( G_i^{gb} y_i^{gb} \right) \left( u_i^{gb} d_i - R_i^{gb} \phi_i^{gb} \right) A, \quad i = 1, \ldots, NCg
\]  

\[
0 = -\frac{\partial}{\partial z} \left( G_i^{gb} \rho_i^{gb} \right) - \rho_i^{gf} d_i A
\]

Fig. 1. Simplified flowsheet of the pilot plant at Paderborn University in a closed-loop configuration, adapted from Hüser and Kenig (2014).
In addition to the volumetric liquid holdup \( \phi^L \), pressure drop \( \Delta p \) is evaluated using the correlation of Billet and Schultes (1999) and the effective phase interface \( \delta^e \) is estimated by the correlation of Tsai et al. (2011).

2.1.2. Film phases

The transport phenomena within the film are commonly considered as a steady-state problem (Kooijman and Taylor, 1995). The key assumptions of the film model result in the one-dimensional mass transport normal to the interface (\( \eta \)-coordinate), and hence, the differential component balance equations comprising simultaneous mass transfer and reaction have the following form:

\[
\sum_{i=1}^{NC^G} y_{i} = 1
\]

\[
\phi^L + \phi^G = 1
\]

\[
0 = \frac{1}{\phi^L} \frac{\partial \phi^L}{\partial \eta} + R_{i}^L, \quad i = 1, \ldots, NC^G
\]

\[
0 = \frac{1}{\phi^G} \frac{\partial \phi^G}{\partial \eta} + R_{i}^G, \quad i = 1, \ldots, NC^G
\]

In dilute electrolyte systems, component fluxes \( n^i \) can be determined with the Nernst-Planck equation (Taylor and Krishna, 1993):

\[
\sum_{i=1}^{NC^G} \sum_{j=1}^{NC^L} n_{ij}^H = -c^G \left( \frac{\partial}{\partial \eta} \frac{\partial F}{\partial \phi} + \frac{\partial F}{\partial \phi} \right) + x_{ij} \delta^G, \quad i = 1, \ldots, NC^G
\]

The inclusion of the electrical potential requires an additional condition of the electroneutrality to be fulfilled in the liquid phase:

\[
\sum_{i=1}^{NC^L} x_{i} = 0
\]

In the gas-film region, the component fluxes are described by:

\[
\sum_{i=1}^{NC^G} x_{i} = 0
\]

\[
x_{i} \delta^G (\eta^L = 0) = \chi_{i}^G, \quad x_{i} \delta^G (\eta^L = 1) = \chi_{i}^L, \quad i = 1, \ldots, NC^G
\]

\[
x_{i} \delta^G (\eta^L = 0) = \chi_{i}^G, \quad x_{i} \delta^G (\eta^L = 1) = \chi_{i}^L, \quad i = 1, \ldots, NC^L
\]

The heat fluxes in the film regions are given by:

\[
q^L = \frac{\chi^L}{\phi^L} \frac{\partial T^L}{\partial \eta} + \sum_{i=1}^{NC^G} n_{i} R_{i}^L
\]

\[
q^G = \frac{\chi^G}{\phi^G} \frac{\partial T^G}{\partial \eta} + \sum_{i=1}^{NC^G} n_{i} R_{i}^G
\]
m_{in} = m_{out} = m'_{j}, \quad j \in \{h, c\} \tag{19}

\dot{V}_{\alpha j}^{\pm} \frac{dT_{\alpha}}{dt} = \dot{m}_{\pm}^{\alpha} \left( T_{\alpha \text{in}} - T_{\alpha \text{out}} \right) + A_{\alpha} \alpha(T_{\alpha}^\gamma - T_{\alpha}^\delta), \quad j \in \{h, c\} \tag{20}

where $\alpha$ is the heat transfer coefficient and $A_{\alpha} = b \cdot \alpha s$ the heat exchange area. The superscripts $w/h$ and $w/c$ refer to the temperatures on the boundaries between the wall (plate) and the hot and cold fluid, respectively.

Bobić et al. (2020) validated their model using experiments with pure water, both as a hot and a cold fluid. Thus, no reaction terms were considered in the mass and heat balance equations. In contrast, our model should be applicable to multicomponent liquids in which reactions take place. Due to the reactions, the liquid composition changes and the wall, considering the assumption of quasi-steady heat transfer in the $x$-direction as shown in Fig. 3 on the right side, the temperatures $T_{w/h}^\gamma$ and $T_{w/c}^\gamma$ must be expressed as:

$$T_{w/h}^\gamma = T_n^\gamma - \frac{k}{\alpha_{\alpha}} (T_n^\gamma - T_n^\delta), \quad j \in \{h, c\} \tag{24}$$

where the corresponding heat transfer coefficients of the hot and cold side are given with the following relation:

$$\frac{1}{k_n} = \frac{1}{\alpha_{\alpha}} + \frac{\delta^g}{2 \lambda_{\alpha}}, \quad j \in \{h, c\} \tag{25}$$

The heat transfer coefficient $\alpha_{\alpha}$ depends on the thermal conductivity of the fluid $\lambda$, the Nusselt number $Nu$ and the hydraulic diameter $d_h$ as:

$$\alpha_{\alpha} = \frac{\nu_d}{Nu}, \quad j \in \{h, c\} \tag{26}$$

The correlation for the Nusselt number depends on the shape of the plate. In case of corrugated plates, the correlation of Martin et al. (2019) is recommended.

### 2.2.1. Types of plate HE

Industrial plate HEs usually consist of about 100 plates, with alternate flow of hot and cold fluids between them. Thereby, a counterflow, a co-current flow and combinations of both are possible. In Fig. 4a and b, two examples of different plate HEs with $N_{plate} = 9$, resulting in 8 channels for the fluid flows, are given. In order to distinguish the differences between the HEs shown in Fig. 4, the following definitions are used according to Martin et al. (2019):

- **Channel (ch):** A channel is the space between two plates.
- **Passage (pg):** A passage is an arbitrary number of channels in which the fluid (hot or cold) flows in parallel (in $x$-direction).
- **Side:** A side refers to the entirety of all channels through which the same fluid flows. Each plate HE consists of two sides (hot fluid side/cold fluid side).

Consequently, various types of plate HEs can be described using the following nomenclature: $(pg, x \ ch_1) / (pg, x \ ch_2)$, while $ch_1$ is the number of parallel hot flow channels that pass the HE $pg_1$, and a similar nomenclature applies to the second side. Thus, Fig. 4a shows a $(1 \times 4 / 1 \times 4)$ plate HE (ideal counterflow), while Fig. 4b depicts a $(2 \times 2 / 2 \times 2)$ plate HE. The $(2 \times 2 / 2 \times 2)$ plate HE consists on each side of a series connection of two passages, with two parallel channels each.
and heat flow directions is illustrated. In order to model different types of plate HEs with different flow patterns, the 1D heat transfer model, presented in Section 2.2, would have to be used to calculate every single heat flow rate $Q$ (shown with crosshatched arrows in Fig. 5) separately. This will result in a very high number of equations to be solved when simulating plate HEs consisting of about 100 plates. In order to reduce the computational effort, the heat flow rates $Q$ can be estimated per passage rather than per plate. This is realized with the HE discretization shown by the dashed black lines in Fig. 5. Within each of the resulting stages, the 1D heat transfer model is applied. In order to calculate the heat flow rate per stage, the heat exchange area of all plates $N_{\text{plate}}$, as well as the total volume and hydraulic diameters of all channels $N_{\text{ch,\text{a}}}$ inside the stage must be determined. For the case that both sides have the same number of channels, we obtain:

$$N_{\text{plate},\text{a}} = N_{\text{plate}} - 1 - N_{\text{pg}} \quad N_{\text{ch,\text{a}}} = N_{\text{ch,\text{a}}} - 1 \frac{N_{\text{pg}}}{2}$$  \hspace{1cm} (27)$$

Assuming that the fluid flow rate in $z$-direction in all hot channels is the same and that this is true for all cold channels, the total heat exchange area, total volume and hydraulic diameter of the stage can be determined by:

$$A_h = N_{\text{plate},\text{a}} h \Delta z, \quad V_i = N_{\text{plate}} V_{\text{ch},i}, \quad V_i^\ast = A_h \Delta z$$

$$d_i = N_{\text{ch,\text{a}}} d_{\text{ch},i}, \quad j \in \{h,c\}$$  \hspace{1cm} (28)$$

resulting in three average temperatures for the hot fluids $T_{h}^\ast$, cold fluids $T_c^\ast$, and the plates $T_p^\ast$ in each stage.

For plate HEs with $N_{\text{pg}} > 1$, the ideal counterflow is disturbed through the turn of the flow direction inside the HE. In the example shown in Fig. 5, the fluids along the 5th plate flow co-currently. It is also possible that the temperature of the cold side is already higher than the temperature of the hot side, so that the heat flow rate through the 5th plate is reversed (from the cold side to the hot side), resulting in lower efficiency of the plate HE. However, the lower effectiveness must be accepted if the ideal counterflow plate HEs cannot be installed in the plant due to the design. In order to model the thermal coupling between the hot and cold side through the 5th plate, Eq. (23) for a single plate is used.

2.3. CSTR model

The CSTR (continuous stirred tank reactor) model is typically used to describe the fluid dynamic behavior of a liquid-phase flow with defined holdup; it is applied for various plant components in this work (see Table 1). The CSTR is a batch reactor with ideal mixing conditions, shown in Fig. 6a.

The amount of CSTR residuals is significant, which leads to an additional conversion in the case of chemical reactions and influences the process dynamics. The corresponding material and energy balance equations are as follows:

$$\frac{d(V_i x_i)}{dt} = \sum L_{\text{in}} x_{i\text{in}} - L_{\text{out}} x_{i\text{out}} + R_i V_i \quad i = 1, ..., NC$$  \hspace{1cm} (29)$$

$$\frac{d(V_i h_i)}{dt} = L_{\text{in}} h_{i\text{in}} - L_{\text{out}} h_{i\text{out}} \pm \dot{Q}$$  \hspace{1cm} (30)$$

where changes of the CSTR residuals $V$ are taken into account.

In the case of an evaporator, the heat supply $\dot{Q}$ is added in Eq. (30). It leads to partial evaporation of the liquid. Assuming thermodynamic equilibrium, the vapor composition can be determined by equilibrium relationships. The gas holdup is neglected due to the low gas-phase density. By using the enthalpy in the energy balance equation, the phase change enthalpy and reaction enthalpy are directly taken into account. All chemical reactions in the solvent can be considered as instantaneous due to the high temperatures in the evaporator (Huepen and Kenig, 2010).

Fluid flow in a single CSTR tends to strong backmixing. The fluid particles do not necessarily move through the CSTR with the same velocity, resulting in a broad residence time distribution. This is a common behavior of plant elements in which the liquid movement is slow, e.g.,. in the column bottoms (Schneider et al., 1999). For plant elements with high fluid velocities, e.g., in the pipeline, narrow residence time
Correlations used in this paper for the determination of the reaction rate

Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( k_{f, i} )</th>
<th>( k_{b, i} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( 1.33 \times 10^{37} \exp \left( \frac{55470.91}{RT} \right) )</td>
<td>( 3.02 \times 10^{-34} \exp \left( \frac{-41264.26}{RT} \right) )</td>
<td>Pinsent et al. (1956)</td>
</tr>
<tr>
<td>R2</td>
<td>( 6.63 \times 10^{34} \exp \left( \frac{-107416.54}{RT} \right) )</td>
<td>( 5.52 \times 10^{-33} \exp \left( \frac{-69157.56}{RT} \right) )</td>
<td>Hikita et al. (1977)</td>
</tr>
</tbody>
</table>

The developed dynamic model was implemented into the commercial software tool Aspen Custom Modeler® (ACM). The model comprises a system of partial differential and algebraic equations (PDAE). A dis-
cretization with respect to the axial $z$-coordinate and normal $y$-coordinate has been carried out, resulting in a differential and algebraic equations system (DAE). Grid independence studies were carried out to determine the number of axial stages and film elements in the column model as well as the number of stages in the 1D heat transfer model for the plate HEs. These numbers were gradually increased until the simulation results showed no significant changes. In order to check whether this state is reached, one parameter obtained from the simulation results was monitored as a function of the number of stages. For the absorption resp. desorption column, grid independence was controlled with the absorption (desorption) efficiency determined as follows:

$$
\Psi = \left( \frac{G_{\text{in},\text{CO}_2} - G_{\text{out},\text{CO}_2}}{G_{\text{in},\text{CO}_2}} \right) \cdot 100\% \tag{34}
$$

It is the most important parameter for evaluating the absorption/desorption performance. For the plate HEs, the outlet temperature of the hot fluid was chosen to check grid independence. The physical properties are determined with the Aspen Properties database as a function of temperature, pressure and composition.

The simulated and experimental results for the first experiment are shown in Fig. 7. In Fig. 7a, the inlet gas and solvent mass flow rates are depicted that illustrate the changes performed. The first change in solvent mass flow rate from 150 to 100 kg/h was made at 0.18 h and is shown with a vertical dashed line (black) in Fig. 7. The second vertical dashed line (black) at 0.79 h represents the change back to 150 kg/h. In Figs. 7b and c, the inlet and outlet temperatures in the desorption and absorption column are shown. Due to the reduced solvent mass flow rate, the constant heat supply in the evaporator leads to higher temperatures of the solvent leaving the desorption column (Fig. 7b). Due to the larger diameter of the desorption column (see Table 4), its holdup is large resulting in a longer transition behavior. After passing the HEs, the solvent with higher temperature leaving the desorption column is cooled down and enters the absorption column (Fig. 7c). The measured inlet solvent temperature of the absorption column decreases after the reduction in mass flow rate from 150 to 100 kg/h, whereas no significant change of the simulated inlet temperature can be observed. In addition to the evaporator heat supply, the solvent is heated by the reactions taking place in the absorption column. The simulated outlet temperatures of the absorption column shown in Fig. 7c are slightly lower than the measured values but show the same qualitative course. Fig. 7b shows peaks in the measured inlet solvent temperature of the desorption column after the change in solvent mass flow rate, especially after the change back to 150 kg/h, which the simulation cannot reproduce. Nevertheless, qualitative agreement between the simulated and measured process dynamics is obvious and the outlet temperatures in the solvent and gas phases are well captured by the simulations.

In Fig. 7d, the gas-phase CO$_2$ concentrations at the absorption column outlet are given. Due to the reduced solvent amount after the first change, the outlet CO$_2$ gas concentration increases. Along with the full dynamic model, the simulations were carried out with the reduced model that does not include the dynamic behavior of liquid distributors, column bottoms and periphery (state-of-the-art model). The deviation between the measured and simulated CO$_2$ concentration, obtained with the full dynamic model, is determined by:

$$
e = \left( \frac{\text{CO}_2,\text{exp} - \text{CO}_2,\text{sim}}{\text{CO}_2,\text{exp}} \right) \cdot 100\% \tag{35}
$$

and shown in Fig. 7d. Within the full simulation time, the deviation of the full dynamic model remains below 5%, which is a very good

### Table 3
Correlations used in this paper for the determination of the equilibrium constant: $\ln K_a = a + \frac{b}{T} + c T + d n T$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R3</td>
<td>0.7996</td>
<td>-8094.81</td>
<td>0.0</td>
<td>-0.007484</td>
<td>Austgen et al. (1989)</td>
</tr>
<tr>
<td>R4</td>
<td>216.049</td>
<td>-12431.7</td>
<td>-35.4819</td>
<td>0.0</td>
<td>Austgen et al. (1989)</td>
</tr>
<tr>
<td>R5</td>
<td>132.899</td>
<td>-13445.9</td>
<td>-22.4773</td>
<td>0.0</td>
<td>Austgen et al. (1989)</td>
</tr>
</tbody>
</table>

### Table 4
Pilot plant data.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount [-]</th>
<th>Length [m]</th>
<th>Diameter [m]</th>
<th>Area [m x m]</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-C</td>
<td>1</td>
<td>3.0</td>
<td>0.02</td>
<td>-</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>C-D</td>
<td>1</td>
<td>7.0</td>
<td>0.02</td>
<td>-</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>D-C</td>
<td>1</td>
<td>3.0</td>
<td>0.02</td>
<td>-</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>E-F</td>
<td>1</td>
<td>7.0</td>
<td>0.02</td>
<td>-</td>
<td>Stainless steel</td>
</tr>
</tbody>
</table>

### Table 5
Conditions and compositions of the gas and solvent entering the absorption column.

<table>
<thead>
<tr>
<th>Component</th>
<th>First experiment</th>
<th>Second experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw gas</td>
<td>Solvent</td>
<td>Raw gas</td>
</tr>
<tr>
<td>Mass flow rate [kg/h]</td>
<td>40.2</td>
<td>150 (100)</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>295.45</td>
<td>288.65</td>
</tr>
<tr>
<td>MEA concentration [wt.-%]</td>
<td>0</td>
<td>25.32</td>
</tr>
<tr>
<td>CO$_2$ concentration [vol.-%]</td>
<td>7.28</td>
<td>-</td>
</tr>
</tbody>
</table>
agreement. The strong influence of the additional holdups in the closed-loop process is obvious, and thus, it is necessary to consider this influence in order to achieve a good agreement between the measurements and simulations. Taking only the holdup in the packings into account results in a large discrepancy and, in essence, in a completely different simulated transient behavior after changing the solvent mass flow rate than in reality. As it is seen in Fig. 7d, the outlet CO$_2$ gas concentration increases only for few seconds and then drops significantly. This can be explained by the reduced loading of the solvent entering the absorption column due to the higher temperature of the solvent in the evaporator. The solvent with the lower loading enters the absorption column and is capable of capturing more CO$_2$ thus improving absorption. This influence of the lower loading of the solvent entering the absorption column on the process can be seen in the full dynamic model after some time necessary for the solvent to pass the desorption column, evaporator and the periphery between the desorption and the absorption column. In Fig. 7d, the time, at which the outlet CO$_2$ gas concentration starts decreasing, can be identified at 0.34 h.

In Fig. 8, the results for the second experiment are shown. They are largely comparable with those of the first experiment, and the strong influence of the liquid distributors and the periphery on the dynamic process behavior can be clearly seen. Due to the slightly lower inlet CO$_2$ gas-phase concentration (cf. Table 5), also the outlet CO$_2$ concentrations in Fig. 8d are lower than in the first experiment. In contrast to the first experiment, the simulated initial steady-state deviates from the measurement by 5%. Furthermore, the deviations following the change in mass flow rate are slightly higher here, especially after the first change in mass flow rate. The increase of the outlet CO$_2$ gas concentration, due to the reduced solvent mass flow rate, is in the measurement much higher than in the simulation. The deviations here are in the range of 5–8%, yet still sufficiently low.

In Fig. 8b and c, qualitative courses of the inlet and outlet temperatures similar to those of the first experiment can be seen. However, the peak in the measured inlet solvent temperature of the desorption column after the second change is higher. The peaks are probably encountered due to the pumps that move the loaded solvent to the desorption column and whose dynamic behavior is not considered in the model. Nevertheless, the good agreement between the simulation and measurement results is confirmed with the second experiment, too.

5. Conclusions

In this work, a novel dynamic model of the overall closed-loop absorption/desorption process including the periphery as well as non-separating column internals of the pilot plant was developed and validated against experimental data obtained in the pilot plant at Paderborn University. The chemical absorption of CO$_2$ with aqueous MEA solutions was used as an example system. The solvent mass flow rate was changed to generate dynamic system responses. Two experiments were carried out. Despite the high complexity of the dynamic model, both the outlet gas-phase concentration and the inlet and outlet temperatures in the columns could be well captured. The deviation between experimental and simulated outlet gas concentrations obtained with the full dynamic model is below 5% for the first experiment and below 10% for the second experiment. The validation performed in this work is a first comprehensive, transparent check of a dynamic closed-loop model for chemical absorption of CO$_2$ with MEA using full set of experimental data. A strong influence of the column internals and the periphery on the dynamic process behavior is demonstrated.

The model was developed in a general form to be applicable to
different chemical absorption systems. In this way, systems containing toxic or carcinogenic gas components can also be investigated, which helps to prevent hazardous situations through leaking into the environment. With the suggested model, dynamic simulations can be performed for any changes (disturbances) in the plant yielding information which is difficult to obtain experimentally. For instance, causes for hazardous situations and ways to their possible elimination can be investigated and the duration between a malfunction and the relevant system reaction can be determined. This knowledge of the dynamic process behavior will help to enhance safety of industrial absorption plants. The functional properties of measurement and control devices can be evaluated with respect to their ability to ensure a regular process operation in case of malfunctions. Should not this be possible, additional control strategies can be proposed based on the simulation results.

In the future work, the validated model will be used to analyze the dynamics of the chemical absorption of coke oven gas in response to various plant disturbances. The coke oven gas contains toxic components, such as hydrogen sulfide or ammonia, which represent a great hazard when leaking into the environment. Simulation studies of the various plant disturbances should help to develop efficient strategies preventing hazardous situations.

CRediT authorship contribution statement

Mike Bothe: Conceptualization, Methodology, Software, Validation, Writing – original draft. Iman Hami Dindar: Investigation. Nicole Lutters: Writing – review & editing. Eugeny Y. Kenig: Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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