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Examination of Hazardous Situations in Industrial Closed-Loop Processes Using Dynamic Simulations

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Closed-loop processes are widely used in the chemical industry, for example in separation processes to recycle waste streams. However, the recycled streams represent a source of instability, especially when the overall system suffers a (desirable or undesirable) change in the operating conditions. In this case, the time required to reach a steady state is significantly longer, because of oscillations encountered in the leaving stream characteristics. The dimensions of such oscillations can reach high and even hazardous values, even if the new steady state is reached in a safe operating condition. This is why the knowledge of the dynamic closed-loop process behavior is essential to prevent hazardous situations. In this work, a general rate-based model of a closed-loop chemical absorption process is presented and the results of dynamic simulations are compared with published experimental data on absorption of carbon dioxide with aqueous monoethanolamine solution. The periphery is considered using dynamic models of the liquid distributors, the liquid holdup in the bottom of the columns as well as of the relevant heat exchangers and pipelines. Based on the simulations, the influence of different closed-loop process elements on the dynamic behavior of the overall configuration can be evaluated, enabling a cause-effect analysis of hazardous situations.

1. Introduction

Chemical absorption is a separation technology widely used in the process industries. The main absorption unit is usually complemented by a desorption unit to regenerate the solvent, thus building a closed-loop configuration. In addition to the absorption and desorption columns, several heat exchangers (HEs) and the periphery (e.g., pipelines) are involved. An example of such a configuration is given in Figure 1. Each of the elements shown in the loop 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 these problems, dynamic process behavior must be well captured.

While reliable steady-state models of closed-loop chemical absorption processes are available, significant gaps exist in the description of the process dynamics. These gaps are related to some factors which have a significant influence on the transient behavior yet can be neglected when a steady-state operation is considered. Among them are the impact of liquid distributors, the liquid holdup in the column bottoms and the pipelines. The simplified HE modeling using a logarithmic temperature difference or even as an equilibrium stage can be judged as sufficient for the steady-state mode (Huepen and Kenig, 2010), but it is not true for the transient regime. In the only publication on the dynamic modeling of a closed-loop absorption/desorption process we could find in the literature (Harun et al., 2012), no liquid distributors and pipelines are included into consideration and no dynamic model validation is performed. Up to now, validated transient models have been published only for single units, e.g., for an absorption column with liquid distributors and with the account of the bottom holdup (Schneider et al, 1999). Models for single HEs governing the process dynamics were published by different authors, e.g., by Correa and Marchetti, (1987) for a shell-and-tube HE and by Bobič et al. (2020) for a plate HE. However, transient models of single units do not guarantee the overall process capture. For this reason, we developed and validated a novel model for the dynamic simulation of the overall closed-loop process which is presented in this paper.

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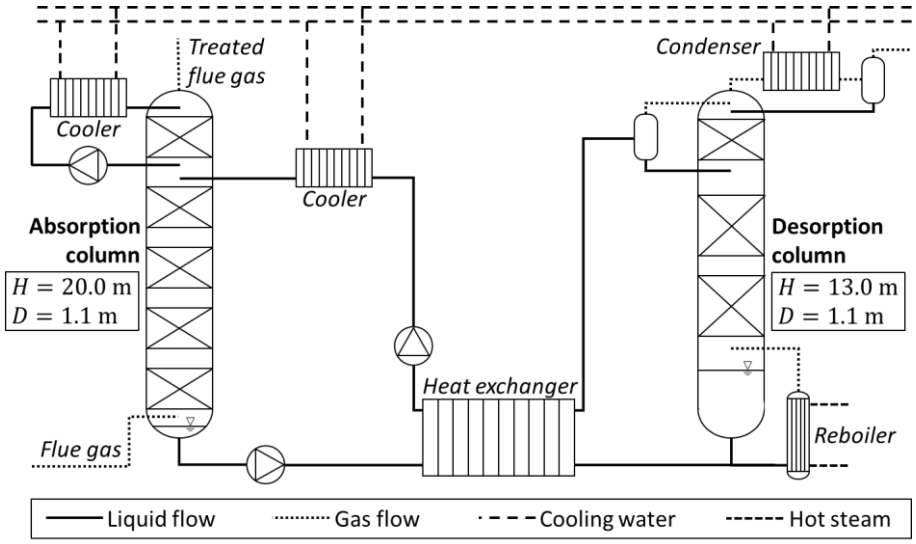

Figure 1: Pilot plant for chemical absorption of CO_2 with monoethanolamine solution (MEA) in Esbjerg, Denmark, according to Faber et al. (2011)

2. Dynamic modeling of the closed-loop process

The model of the closed-loop process comprises the descriptions of the single elements of the closed-loop configuration. These descriptions are given in the following sections, while both columns are treated as packed columns.

2.1 Columns

The packing elements are jointed to build a packed bed, while liquid distributors are installed between these beds to ensure an even distribution of the solvent across the column cross-sections. The liquid solvent enters at the top of the column and flows down through the packed beds and distributors. The gas enters at the bottom of the column and flows upwards counter-currently to the liquid stream. The desorption column has a reboiler which supplies heat for the regeneration of the loaded solvent and a condenser.

As in the previous work by Huepen and Kenig (2010), chemical absorption and desorption of the solvent are modeled using the rate-based approach. In this approach, the column stages are described with the film theory, while each contacting phase is subdivided into a bulk and a film region. Mass and heat balance equations are formulated for both regions, while diffusion and kinetically controlled chemical reactions take place only in the films. Thermodynamic equilibrium is assumed at the phase interface. To account for the process dynamics, the gas-bulk and liquid-bulk mass and heat balance equations should be extended by the relevant holdup terms. However, the influence of the gas-bulk holdup can be neglected because of the much lower density compared to the liquid. The corresponding holdup terms in the film regions can be neglected due to their much smaller holdups compared to the bulk phases (Schneider et al., 1999).

The liquid distributors have a great influence on the dynamic behavior due to their significant holdup. To model a liquid distributor, the mass and heat balances are set up according to a continuous stirred tank reactor (CSTR), model, as proposed by Schneider et al. (1999). To determine the holdup of the solvent, the knowledge of the geometry and the filling level of the distributor is necessary.

At the bottom of both columns, the liquid is usually kept at a stable level to ensure some constant holdup. This holdup is taken into account, again, by using a CSTR model.

2.2 Heat exchangers

There are numerous types of HEs used in the chemical industry, the most common ones being the plate HE. If a phase change takes place, for example in the condenser or reboiler, shell-and-tube HEs are mostly used. The efficiency of the heat transfer can be increased by additional internals or special geometries of the HE, so that a wide range of specifications is possible. Here, we use a general modeling approach to capture the dynamic behavior of HEs.

In Figure 2a, a conventional shell-and-tube HE is sketched. Baffles are usually installed to prevent dead zones, allowing the shell-side fluid to flow through the HE in a meandering pattern. Both for the tube-side and for the shell-side fluid, multiple passes can be realized in the HE to increase the residence time of the fluids. This would

enhance the efficiency of the HE. In the variant shown in Figure 2a, an example of a shell-and-tube HE with one shell pass and two tube passes is given, a so-called *1–2 shell-and-tube HE*. In order to be able to take the flow characteristics into account, the method of Gaddis and Schlünder (1979) is used. The shell-and-tube HE is subdivided into cells at the baffles and tube passes, as illustrated in Figure 2b. Later, Correa and Marchetti (1987) developed and validated a dynamic model, in which the cells are used as a grid for the mass and heat balances of the fluids (cf. Figure 2c).
In a plate HE, the hot and cold fluids flow through the channels between the plates in an alternate mode. Figure 2d shows a scheme of a plate HE with a countercurrent flow. Bobič et al. (2020) developed and validated a dynamic model for the plate HE, which is similar to the shell-and-tube HE model of Correa and Marchetti (1987). As shown in Figure 2d, the plate HE is subdivided into separate cells along the plate length, which are used as a grid to formulate the mass and heat balances.
In our work, the model of Correa and Marchetti (1987) for to the shell-and-tube HE and the model of Bobič et al. (2020) for the plate HE are used as a part of the description of the closed-loop process presented. The required number of the cells for both HEs is determined by a grid independence study.

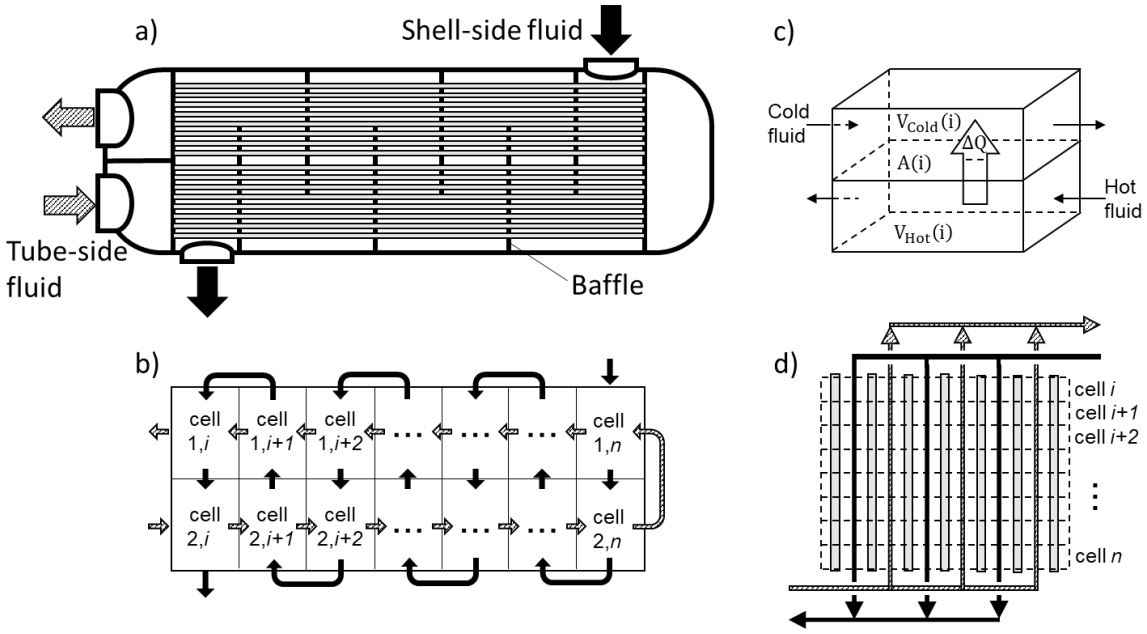

Figure 2: Schematic of a 1–2 shell-and-tube HE (a) with a subdivision into separate cells according to Gaddis and Schlünder (1979) (b), a control volume of a single cell according to Correa and Marchetti (1987) (c) and a schematic design of a plate HE with cells according to Bobič et al. (2020) (d)

2.3 Periphery

In addition to the units considered, the dynamic behavior of the closed-loop process is influenced by the periphery. The latter includes, among other equipment, the pipelines. An ideal fluid dynamic behavior of a pipeline corresponds to a step response after a time delay. A non-ideal hydrodynamic behavior leads to a certain dispersion due to axial backmixing, which can be approximated with a CSTR cascade (Westerterp et al., 1984). The total pipeline volume may be modeled by several CSTR. The higher the number of CSTR is, the closer is the approximation to the ideal dynamic behavior.

3. Dynamic simulations

To carry out dynamic simulations, all models described above were implemented in the commercial software tool Aspen Custom Modeler® (ACM). Besides, the Aspen Properties database (eNRTL) was integrated to determine the properties of the pure components and mixtures depending on temperature, pressure and (for mixtures) on concentration.

3.1 Case study

The closed-loop process shown in Figure 1 was used as an example of an industrial plant configuration. In the related paper by Faber et al. (2011), experimental results for different step responses during the chemical absorption of CO_2 with MEA were published. To simulate this process, rates of the chemical reactions must be

known. The reactions can be characterized by the two-step mechanism, whereby an amine reacts with CO_2 forming a zwitterion as an intermediate (Vaidya and Kenig, 2010). The overall reaction system includes a set of five parallel and consecutive reactions in the liquid phase, while in the gas phase no reactions occur (Kucka et al., 2003). According to Taylor and Krishna (1993), the Nernst-Planck equation can be used to describe multicomponent diffusion for dilute electrolyte solutions.
For the step responses, the pilot plant was initially brought in a steady state. In all experiments, this steady state was nearly the same. Afterwards, an inlet variable was changed abruptly, and the dynamic transition behavior was monitored based on the outlet variables until a new steady state was reached.
The dimensions of the absorption and desorption columns given by Faber et al. (2011) were implemented in the model used in our work. The absorption column consists of four consecutive packed beds with a packing height of 4.25 m each and one washing section at the top with a height of 3 m, all equipped with Mellapak 2X. The purpose of the washing section is to reduce solvent losses and to control the water balance of the process. The desorption column consists of two 5 m beds and a washing section of 3 m height, filled with IMTP50 random packing. Both columns have an inner diameter of 1.1 m. The HE between the absorption and desorption column is a plate HE.

3.2 Determination of missing data

Assumptions had to be made in the model because of missing plant information. The missing data include the specifications of the HEs and the periphery. Also, no information on the liquid level in the distributors and in the bottom of the columns is available. To estimate the missing data, the following assumptions are made.
First, both the solvent cooler and the washing liquid cooler of the absorption column (cf. Figure 1) were assumed to be plate HEs, whereas the condenser and reboiler were assumed to be shell-and-tube HE. The geometrical data of all HEs used in the studied configuration is not available and some guesses have to be made. Valuable information regarding the geometry and optimal functioning of shell-and-tube HEs could be found in Theodore (2011), e.g., value ranges for the tube diameter, wall thickness, fluid velocities, etc.
Further on, some temperatures of the fluids at steady state given by Faber et al. (2011) could be used to refine the geometrical parameters within the ranges suggested by Theodore (2011). Specifically, we used the temperatures of the fluids entering and leaving the HEs.
In the paper by Faber et al. (2011) the total reboiler heat flow rate as well as the corresponding entering steam flow are given. Our calculations indicate that the value of the heat flow rate agrees with the entering steam flow under assumption of total isothermal condensation. By using the heat flow rate as a given input, the reboiler (a shell-and-tube HE) can be modeled in a simplified way as a single CSTR with the added heat as a source term.
The liquid distributors were assumed to be sieve trays with the liquid dripping down through the sieve holes. When the total area of all sieve holes is given, the outlet mass flow rate can be determined as a function of the liquid level on the sieve using the Torricelli equation. For the hole size and hole density of the sieve, characteristic values determined by the company Sulzer (2021) as a function of the liquid load can be used. Based on the liquid load at the initial steady state, this results in a hole diameter of 4 mm and a density of 200 holes per square meter. The holdup in the liquid-bulk balance is determined based on the liquid level on the sieve obtained from the Torricelli equation and on the cross-section of the column.
Finally, the liquid level in the bottom of both columns and the total volume of the pipelines have to be assumed. These values were fitted based on the dynamic process behavior in the experiments of Faber et al. (2011). The estimations for the missing data are summarized in Table 1, where $n_{\text{plates/tubes/CSTR}}$ represent the amount of plates, tubes and CSTR. These values were kept unchanged for the dynamic simulations of all experiments.

3.3 Step responses

In the experimental investigations of the dynamic closed-loop process behavior, Faber et al. (2011) changed three inlet variables, the flue gas flow rate, the solvent flow rate and the steam flow rate in the reboiler. Three different experiments were carried out. In the first two experiments, the flue gas flow rate and the solvent flow rate were reduced separately, while the other inlet parameters were kept constant. The reduction of the solvent flow rate was achieved by opening a valve placed before the solvent inlet of the absorption column. In the last experiment, all inlet flow rates (gas, solvent, steam) were reduced simultaneously. An overview of the changes in the experiments is given in Table 2. The changes in the inlet flow rates in the experiments were used to perform the dynamic closed-loop simulations. The initial steady state of the process is simulated for 900 s (15 min), afterwards the inlet flow rate was changed abruptly and the transient process behavior was simulated for a total time of 7,200 s (2 h). The measured outlet CO_2 concentrations in the treated flue gas from Faber et al. (2011) and the corresponding simulated values for all three experiments are given in Figure 3. The simulation time took 40-50 h for one dynamic simulation of the overall closed-loop process.

Table 1: Estimated values for the missing data

Units	Total volume (m^3)	n_{plates} (-)	n_{tubes} (-)	n_{CSTR} (-)
Bottom of absorption column	0.33	-	-	1
Bottom of desorption column	0.33	-	-	1
Pipeline	0.50	-	-	100
Heat exchanger	0.20	151	-	-
Solvent cooler	0.15	101	-	-
Washing liquid cooler	0.06	41	-	-
Condenser	0.08	-	62	-
Reboiler	0.05	-	-	1

Table 2: Experimental data of Faber et al. (2011)

Inlet flows	Experiment 1	Experiment 2	Experiment 3
Flue gas flow rate(m^3/h)	5,000 → 3,500	5,000	5,000 → 4,000
Solvent flow rate (m^3/h)	18	18 → 14.4	18 → 14.4
Steam flow rate (m^3/h)	1,820	1,840	1,840 → 1,500

Figure 3 shows that the simulation and experimental results are in a qualitatively satisfactory agreement for all three experiments. The graphs for the first experiment in Figure 3a indicate that the reduction of the flue gas flow rate leads to a decreased CO_2 concentration. The reason is that the amount of CO_2 in the gas is lower, while the amount of CO_2 absorbed by the solvent is nearly constant. The simulated outlet CO_2 concentration is about 0.3 vol.-% higher than the measured value.

In Figures 3b and 3c, it is seen that the reduction of the solvent flow rate leads to oscillations of the CO_2 outlet concentration. This is because a smaller solvent amount in the absorption column can absorb less CO_2 resulting in an increased CO_2 outlet concentration. In the desorption column, the smaller amount of the loaded solvent is further heated up with a constant heat flow rate, and the solvent is better regenerated. This, in turn, leads to a lower inlet loading of the solvent in the absorption column and more CO_2 can be absorbed decreasing the CO_2 outlet concentration. This alternating interaction begins after some time necessary for the solvent to pass through the whole closed-loop. This time delay can be detected by the interval from the initial change to the first peak in the oscillation (cf. Figure 3b). The time delay took about 20 min in the experiment, while in the simulation, it was about 18 min. Figures 3b and 3c further show that the simulated oscillations have smaller amplitudes and a higher frequency than the measured oscillations. Figure 3c also shows that the new steady state is reached much earlier in the simulations than in the experiment. These deviations are most likely caused by the adjusted specifications, which cannot fully match the specifications of the real process. A further reason could be the non-idealities of the fluid dynamics of the real flow in the experiment, e.g., turbulence or maldistribution in the packings, which were not taken into account by the model. Finally, the differences in Figure 3c could also be caused by the simplified consideration of the reboiler as a CSTR, neglecting the dynamic properties of the steam flow change.

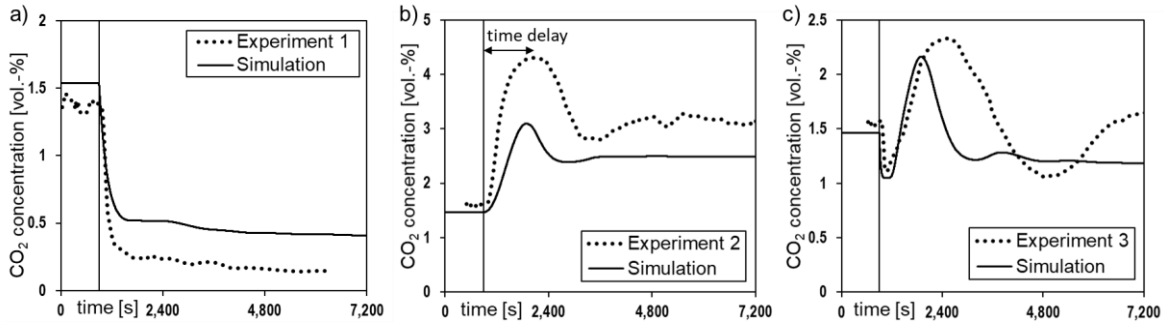

Figure 3: Experimental results of Faber et al. (2011) and the simulation results obtained with our closed-loop model for experiment 1, reduction of the inlet gas flow rate (a), experiment 2, reduction of the solvent flow rate (b) and experiment 3, simultaneously reduction of the inlet gas, solvent and steam flow rates (c)

Despite this disagreement, the first simulation results can be considered as reasonably good, since the complex dynamic behavior of the closed-loop process could be qualitatively captured while the maximum deviation of the outlet CO_2 concentration is found to be below 1.5 vol.-%. In order to be able to perform a further, more accurate validation of the model, we are going to carry out experiments in a pilot closed-loop plant available in

Paderborn University and described in Hüser and Kenig (2014). With these experiments, all specifications of the units and periphery will be known.

4. Conclusions

This work presents a general model for the dynamic simulation of a closed-loop process. As an example, the chemical absorption of CO_2 with MEA was used. First simulation results on the dynamic process behavior were compared with published experimental data obtained at a corresponding pilot plant. In the experiments, the process response on some abrupt changes in the operation conditions was studied. However, for this plant, full data was not available and a part of it had to be assumed based on information about industrially accepted plant equipment. This resulted in some deviations between the simulated and experimental CO_2 concentrations. Nevertheless, the dynamic behavior could be satisfactory represented qualitatively, including typical oscillations in the process behavior. The maximum deviation of the outlet CO_2 concentration is below 1.5 vol.-%. However, despite that the deviation between the simulated and experimental values of the time required for the solvent to pass through the overall loop is small (about 2 min), the new simulated steady state is reached much earlier than in the experiment.
In the future, experiments will be carried out with a pilot plant with known specifications. The model will be further validated on the basis of these measurements and used for the simulation and analysis of hazardous situations, which is important for safe performance of chemical absorption processes. Since CO_2 and MEA do not represent a direct hazard, a different absorption system with toxic gas components will be considered. In addition, the influence of the liquid holdup in the distributors and in the column bottoms as well as the dimensions of different elements on the dynamic closed-loop process behavior will be studied.

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