Optimal design of post combustion CO\textsubscript{2} capture processes based on phase-change solvents

Panagiotis Kazepidis\textsuperscript{a,b}, Athanasios I. Papadopoulos\textsuperscript{a}, Panos Seferlis\textsuperscript{a,b}, Felipe A. Perdomo\textsuperscript{c}, Amparo Galindo\textsuperscript{c}, George Jackson\textsuperscript{c}, Claire S. Adjiman\textsuperscript{c}

\textsuperscript{a}Chemical Process and Energy Resources Institute (CPERI) – Centre for Research and Technology – Hellas (CERTH), Thermi-Thessaloniki 57001 Greece
\textsuperscript{b}Department of Mechanical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
\textsuperscript{c}Department of Chemical Engineering, Centre for Process Systems Engineering, Imperial College London, London SW7 2AZ, UK
seferlis@auth.gr

Abstract

The current work addresses the investigation of phase-change solvents behaviour during the design of post-combustion CO\textsubscript{2} capture processes. The use of phase-change solvents leads to energetic gains due to their lower regeneration energy demands. The latter are enhanced in this work by the consideration of systematic structural and operating modifications imposed on a reference absorption/desorption flowsheet. Such modifications are realized with the help of a rigorous and flexible model that can represent the phase-change behaviour and include stream redistribution options that aim to enhance the main process driving forces. An aqueous N-methylcyclohexylamine (MCA) solution is employed in an effort to exploit the solvent’s phase separation behaviour towards the reduction of the total process cost and energy requirements.

Keywords: CO\textsubscript{2} capture, optimal design, phase change solvents, MCA, N-methylcyclohexylamine.

1. Introduction

Solvent-based absorption/desorption processes represent a mature technology for post-combustion CO\textsubscript{2} capture. A major drawback is the high regeneration energy requirements which prohibit the wide industrial adoption of such systems. Phase-change solvent processes are emerging as a new and promising technology which enables up to 50% reduction in regeneration energy requirements (Pinto et al., 2014). This is achieved through the use of solvents which exhibit phase-change behavior due to the appearance of a second liquid phase upon reaction with CO\textsubscript{2} and possibly a subsequent increase of temperature. This enables the use of a physical process usually in the form of a decanter to separate the two liquid phases; one of them can be partially or totally recycled directly to the absorber, whereas the other is transferred to the desorber, resulting in significant energy reduction. Despite the obvious advantages, there is very limited research addressing modelling and design of such systems, leaving considerable space for performance improvements. The very few reported studies pertain to technoeconomic assessment of specific solvents using commercial software, with no systematic optimisation approaches reported to date (Raynal et al., 2011; Pinto et al., 2014).
In this work, a rigorous and flexible model that can represent the phase-change behaviour of absorption/desorption CO\textsubscript{2} capture processes is proposed. The column models are based on the orthogonal collocation on finite elements (OCFE) technique tailored to three phase systems that support a sufficiently accurate but also computationally tractable process representation. The main advantages include the transformation of discrete process characteristics into continuous decision variables, and the ability to represent and track sharp changes of important variables such as concentration and temperature profiles along the column domain. The model is also employed in the context of a superstructure representation which supports optimisation.

2. Methodology

2.1. Modelling framework

The use of phase-change solvents (PCS) systems in CO\textsubscript{2} capture processes provides the opportunity for enhanced performance as well as the reduction of process energetic demands and economic resources through the exploitation of their liquid-liquid phase separation capabilities. The optimum design of three-phase flowsheets is challenging because it requires (a) a systematic modelling approach able to capture transitions between vapour-liquid (VLE) and vapour-liquid-liquid (VLLE) equilibria regimes, and (b) an underlying framework, which is sufficiently flexible to account for the interactions of the large number of the desired structural and operating features.

The modeling framework employed in this work to meet requirement (a) is based on the OCFE approximating technique (Dalaouti and Seferlis, 2006; Damartzis and Seferlis, 2010) to model three-phase reactive separation systems. The separation column is divided into column sections, defined as the column segment between two successive feed or draw streams. A section is further subdivided into finite elements (FE) of variable size. Within each finite element a given number of collocation points (CP) are defined based on the degree of polynomial approximation. These points are selected as the roots of the discrete Hahn family orthogonal polynomials. A finite element is illustrated in Figure 1 (left) with the two liquid and vapour flows leaving and entering the collocation points.

Figure 1: Three-phase OCFE presentation (left), superstructure with indicative placement of liquid-liquid phase separator (right)

Eq. (1) – (5) represent the main equations of a VLLE model with \( NC \) components and \( n \) collocation points under the assumption of a dispersed second liquid phase. Eq. (1) is the
Optimal design of post combustion CO\(_2\) capture processes based on phase-change solvents

material balance and Eq. (3) the energy balance at collocation point \(j\) that corresponds to a location in the column \(s_j\): \(x_{i}^{L1}\) and \(x_{i}^{L2}\) are the molar fractions of each component in the two liquid phases and \(y_{i}^{V}\) is the vapour molar fraction of each component. The reactive absorption is incorporated implicitly in the phase equilibrium model. In Eq. (3) symbol \(H\) represents the enthalpies of each phase and \(\Delta H\) is the heat of reaction. The equilibrium between the vapour and the \(Li\) phase is presented in Eq. (4) by \(K_{i}^{V}\), whereas Eq. (5) is the equilibrium between the two liquid phases, represented by \(K_{i}^{L}\). The dispersed liquid phase (2nd liquid phase) does not interact with the vapour phase and therefore only two interfaces are considered; vapour – liquid \(L1\) and liquid \(L1\) – liquid \(L2\).

\[
L1(s_j + 1) + L2(s_j + 1) - L1(s_j) - L2(s_j) + V_i(s_j - 1) - V_i(s_j) = 0 \quad (1)
\]

\[
x_i^{L1}(s_j) = \frac{L1_i(s_j)}{\sum_{i=1}^{NC} L1_i(s_j)} x_i^{L2}(s_j) = \frac{L2_i(s_j)}{\sum_{i=1}^{NC} L2_i(s_j)} y_i^{V}(s_j) = \frac{V_i(s_j)}{\sum_{i=1}^{NC} V_i(s_j)} \quad (2)
\]

\[
L1_i(s_j + 1)H^{L1}(s_j + 1) + L1_i(s_j + 1)H^{L2}(s_j + 1) + V^V(s_j - 1)H^V(s_j - 1) -
L2_i(s_j)H^{L1}(s_j) - L2_i(s_j)H^{L2}(s_j) - V^V(s_j)H^V(s_j) + \Delta H = 0 \quad (3)
\]

\[
y_i^{V}(s_j) = K_{i}^{V}(s_j)x_i^{L1}(s_j) \quad (4)
\]

\[
x_i^{L2}(s_j) = K_{i}^{L}(s_j)x_i^{L1}(s_j) \quad i = 1, ..., NC; \ j = 1, ..., n \quad (5)
\]

2.2. Design framework

The model shown for the column section is directly adapted on the superstructure proposed by Damartzis et al. (2014) for two-phase post-combustion CO\(_2\) capture processes. The superstructure, shown in Figure 1 (right) consists of modules representing generic process tasks (e.g., reactive, separation, heat transfer) and interconnecting streams emulating material flows. Reactive separation and liquid-liquid phase change processes may be represented by different modules through the column section. Additional information is reported in Damartzis et al. (2014) pertaining to heat transfer tasks. Several different modules may be connected in the same flowsheet using a broad set of stream types (e.g., recycle, bypasses and so forth). The proposed generic tasks account for (a) reaction, mass and heat exchange between different phases within each module, and (b) stream mixing and splitting to enable distribution of materials among different modules. This representation enables the reproduction of any potentially desired representation of solvent-based CO\(_2\) capture processes. For clarity, the liquid-liquid separator is illustrated before the heat exchanger in Figure 1 (right), but it can also be placed after the heat exchanger and connected in any desired way to the columns as in Figure 2.

The combination of the superstructure approach with the OCFE representation introduces important advantages in process optimization. The element length becomes a design variable that indicates the number of stages or equivalent packing height in the column. Accordingly, the size of the separation column can be deduced from the sum of element lengths comprising the column plus the discrete stages, if any, such as the distinct feed stages, reboilers and condensers. Hence, the integer variable denoting the number of stages becomes continuous. Further avoidance of integer variables is achieved by the continuous representation of the location of side feed or draw streams in the columns. Temperature and composition profiles in the column are approximated by continuous Lagrange polynomials of position inside the column. Finally, OCFE supports a significant reduction in terms of the total number of model equations without compromising the resolution of the model, by enabling the solution of the material and energy balances of the equilibrium model on a reduced number of collocation points.
3. Implementation

To investigate the effect of PCS on the optimal design of CO₂ capture processes a N-methylcyclohexylamine (MCA) 35 wt% aqueous solution is considered. MCA is a cyclic secondary aliphatic amine, which has been shown to demonstrate enhanced CO₂ capture capabilities (Jeon et al. 2014; Zhuang et al., 2016) is used. The flowsheet investigated in this work is shown in Figure 2. In addition to the absorption and desorption columns a liquid-liquid phase separator is employed to exploit the phase-split exhibited by MCA.

Figure 2: Flowsheet structure used in optimal design.

In the case of MCA, phase separation occurs at 90°C, so the liquid-liquid phase-separator (LLPS) is positioned after the intermediate heat exchanger. In principle, the superstructure may be used to investigate various structural flowsheet options. In this work, for the first time the performance of MCA through systematic process design is investigated and a new structural design option in phase-change flowsheets is explored. After the phase separation, the CO₂-rich phase is directed to the stripper column, whereas the CO₂-lean stream may be recycled entirely or partially to the absorber top through a splitter. The fraction of the CO₂ lean stream leaving the LLPS is a degree of freedom in optimisation. This design option is considered to investigate the trade-off between the regeneration energy requirements and the effects of absorber size on the total process cost. The only flowsheet proposed to date for PCS allows for complete recycle of the CO₂-lean stream to the absorber, leaving the interplay of regeneration energy-absorber size unexplored. A total of seven design decision variables is considered including the split fraction after the LLPS, the pressure in the columns, the reboiler temperature, the amine flowrate as well as the column sizes. The objective function is expressed as the sum of the total process capital and operating expenses as follows:

\[
F = \sum_{i=1}^{N_{\text{cap}}} C_{\text{sep},i} + \sum_{i=1}^{N_{\text{cap}}} C_{\text{HEX},i} + \sum_{i=1}^{N_{\text{pump}}} C_{\text{pump},i} + \frac{C_{\text{steam}} + C_{\text{cool}} + C_{\text{amine}}}{OPEX}
\]

(6)

CAPEX terms reflect the annualized capital costs of the separation, the heat exchangers and the pumping equipment, whereas the OPEX terms stand for the costs of steam in the reboiler, water (both process and cooling) and the fresh amine used in the system. Employed initial conditions as well as process specifications are listed in Table 1.

The CO₂ vapour pressure \(P_{\text{CO₂}}\) in kPa with respect to loading \((a \text{ mol CO}_2 / \text{mol amine})\) and temperature \((T)\) is represented by Eq. (7) which is fitted from experimental VLLE
Optimal design of post combustion CO$_2$ capture processes based on phase-change solvents

data (Tzirakis et al., 2018), with $R^2$ =0.96 for $T=40 \degree C, 60 \degree C$, and $90 \degree C$. For MCA and H$_2$O in the vapour phase ideal behavior is assumed. The heat of reaction ($\Delta H$ in J/mol) is calculated using Eq. (7) derived by a polynomial approximation (Oexmann, 2011):

$$log_{10}(P_{CO2}) = 21.65 - 19.81 \cdot a - \frac{7343}{T} - 75720 \cdot \frac{a^2}{T^2} + 721500 \cdot \frac{a}{T^2} + 5435 \cdot \frac{a}{T}$$ (7)

$$\Delta H = -R \cdot (-7343 - 2 \cdot 75720 \cdot \frac{a^2}{T} + 2 \cdot 721500 \cdot \frac{a}{T} + 5435 \cdot a)$$ (8)

4. Results and discussion

Table 2 presents the optimal solution for MCA (MCA$^{opt}$) compared to an optimal solution obtained for monoethanolamine (MEA) 30 wt %. Two more cases are explored, namely MCA$^1$ and MCA$^2$, where the split fraction after the liquid-liquid phase separator is fixed at specific values, one lower and one higher than the optimal solution. This enables the investigation of the effect of the split fraction in the overall performance.

Table 2: Design optimization results

<table>
<thead>
<tr>
<th>Case</th>
<th>MCA$^1$</th>
<th>MCA$^{opt}$</th>
<th>MCA$^2$</th>
<th>MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$-lean phase split ratio (%) to stripper</td>
<td>20</td>
<td>28.63</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Equivalent Stages:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorber / Stripper</td>
<td>24 / 26</td>
<td>22 / 26</td>
<td>22 / 27</td>
<td>11 / 27</td>
</tr>
<tr>
<td>Reboiler Temperature (K)</td>
<td>376.58</td>
<td>376.87</td>
<td>377.35</td>
<td>393.15</td>
</tr>
<tr>
<td>Phase Split Ratio (%) (rich/lean)</td>
<td>30.63</td>
<td>30.63</td>
<td>30.63</td>
<td>-</td>
</tr>
<tr>
<td>Bottom Pressure (bar):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorber / Stripper</td>
<td>1 / 1</td>
<td>1 / 1</td>
<td>1 / 1</td>
<td>1.9 / 1.8</td>
</tr>
</tbody>
</table>

Figure 3: Both reboiler duty and annual cost of MCA aqueous phase split ratio cases, all values scaled with respect to MEA case, values lower than 1 indicate better performance than MEA.

Optimization results reveal that all the cases using MCA exhibit lower operating pressures in both columns as well as reduced operating temperature in the reboiler than MEA. The
second liquid phase is formed above 363.15 K, so this is the target temperature in the decanter for the liquid-liquid phase separation that must be provided by the heat exchanger. Reduced reboiler duty (2.3 GJ/ton CO₂) by 42.5 % at a lower temperature level by 16.2°C is required in the optimised MCA case compared to the conventional MEA case (4.0 GJ/ton CO₂). This is a significant advantage of the phase-change solvent capture system. When the recycle of the CO₂-lean stream to the absorber increases (i.e. in MCA'), a larger absorber column is needed in order to achieve the overall CO₂ capture specification. A large recycle of the aqueous liquid stream reduces the total amount of CO₂ captured per pass. Eventually, this results in lower regeneration energy, due to lower volume in the desorber, but at a higher investment cost, as shown in Figure 3. MCA performs better even at pressures of 1 bar (thermodynamic data were available only for this pressure). Potential increase of pressure in the desorber would further improve the capture performance.

5. Conclusions

The optimal design of an amine-based post-combustion CO₂ capture process using a phase-change solvent was presented. The process was modelled using a rigorous, equilibrium-based model, able to accurately represent the underlying physical and chemical phenomena, coupled with the OCFE technique for model size reduction. An aqueous MCA solution was used as a representative phase-change solvent, aiming to investigate the impact of phase-splitting behaviour. Stream redistribution possibilities and a flowsheet that takes advantage of the two liquid phases that are formed, were generated using a generalized process design superstructure. Design optimization results indicate a substantial energy reduction in the reboiler and subsequent reduction in the total annual cost compared with a reference plant operating with a MEA solvent, making phase-change solvents a promising alternative for further investigation.

Acknowledgements

This project has received funding from EU Horizon 2020 program under agreement 727503 - ROLINCAP – H2020-LCE-2016-2017/H2020-LCE-2016-RES-CCS-RIA

References