CHEMICAL ENGINEERING TRANSACTIONS

VOL. 35, 2013

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Varbanov, Jiří Klemeš, Panos Seferlis, Athanasios I. Papadopoulos, Spyros Voutetakis

ISBN 978-88-95608-26-6; **ISSN** 1974-9791

DOI: 10.3303/CET1335196

Generalized Framework for the Optimal Design of Solvent-Based Post-Combustion CO_2 Capture Flowsheets

Theodoros Damartzis[a,b], Athanasios I. Papadopoulos[a], Panos Seferlis[a,b,*]

[a]Chemical Process and Energy Resources Institute (CPERI), Center of Research and Technology Hellas (CERTH) 57001 Thermi, Thessaloniki, Greece
[b]Department of Mechanical Engineering, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece
seferlis@cperi.certh.gr

A generalized framework is proposed for the optimal design of post-combustion CO_2 capture processes based on a systemic and flexible equilibrium separation model that employs orthogonal collocation on finite elements (OCFE) techniques. Within this context, a column section of adaptive separation capability and functionality serves as the fundamental structural block for the identification of efficient separation schemes. Separation column sections in combination with heat transfer blocks as well as stream splitters and mixers enable the generation and evaluation of alternative flowsheet configurations within a non-linear optimization program. The main objectives for the flowsheet evaluation involve separation and thermal efficiency that eventually impact the economics of the overall process. The proposed design framework was used for the optimal design of alternative flowsheet configurations for the separation of CO_2 from a flue gas stream using a 30% weight MEA aqueous solution.

1. Introduction

Amine based CO_2 capture processes have gained a dominant role in industrial CO_2 capture applications mainly due to the mature technology they utilize and the high CO_2 loadings that can be obtained. However, a highly competing environment imposes new more stringent specifications on the achieved process targets, especially the induced thermal cost for the CO_2 separation. It is therefore imperative to develop efficient design tools that would enable the improvement of the process performance and reduce the overall penalty for CO_2 capture.

Flowsheet design of amine CO_2 capture has been reported by Jassim and Rochelle (2006) that used a rate-based model to describe the effect of the operating pressure in the thermal and power requirements of the solvent regeneration column using a multi-pressure configuration. Even though rate-based models (Moiola and Pellegrini, 2013) enable the calculation of highly accurate predictions, their employment requires significant design detail about the column such as type of packing material that may not be available at a preliminary process design stage. In addition, the high degree of complexity involved in the model structure may make the design procedure quite cumbersome. On the contrary, equilibrium based models enable easier model formulation and smaller solution times properties that can facilitate enormously the flowsheet design procedure. Oyenekan (2007) used an equilibrium model for the simulation of alternative multi-feed and multi-pressure configurations for the stripper column. Le Moullec and Kanniche (2010) used miscellaneous flowsheet structures investigating their effect on the overall process efficiency. It was concluded that optimal heat and mass integration can provide efficient design solutions. Similarly, Cousins et al. (2011) presented various commercial and other process flowsheets and provided a critical assessment of their performance. Ismail et al. (2001) presented a framework for the synthesis of reactive separation processes, through which process alternatives that explicitly consider heat and mass integration can be formulated. Binary decision variables were used to represent the connectivity among various process streams resulting to a large problem that must be treated with mixed-integer nonlinear programming (MINLP) techniques. Proios and Pistikopoulos (2006) used continuous analogues for the column sections to enable a flexible framework for efficient flowsheet representation.

Please cite this article as: Damartzis T., Papadopoulos A.I., Seferlis P., 2013, Generalized framework for the optimal design of solvent-based post-combustion co2 capture flowsheets, Chemical Engineering Transactions, 35, 1177-1182 DOI:10.3303/CET1335196

The main aim of this work is the development of a generalized framework for the optimal design of efficient CO_2 capture processes. Such a goal is essentially assisted through a systemic and flexible modeling scheme that combines equilibrium-based separation models with the approximating power of the OCFE technique. OCFE modeling technique allows the representation of separation sections with a reduced-order model utilizing polynomial approximation for the key model variables within the column domain. In a nutshell, OCFE enables the description of complex phenomena in a compact way while maintaining good accuracy in model predictions. The fundamental structural block for the separation processes is the column section, which in addition to a heat transfer block, and stream splitters and mixers enable the generation of alternative flowsheet configurations.

2. Structural block models

Separation columns are divided into column sections usually defined as the column parts between two successive feed or product (draw) streams. The representation of the absorption and desorption process that usually takes place in packed column sections is achieved through the consideration of a set of discrete theoretical stages (Kenig and Seferlis, 2009). The set of discrete theoretical stages is then approximated by a compact model formulation through polynomial approximation within an OCFE context. OCFE further divides each column section into a number of finite elements and approximates the process variables, such as the component molar flowrates and stream molar enthalpy rates along the column as continuous functions of position inside the column section. Therefore, the discrete set of theoretical stages is transformed into a continuous analogue. Within each finite element a specific number of collocation points is defined and selected as the roots of the Hahn family of orthogonal polynomials. Collocation points are usually much fewer than the number of the respective theoretical stages represented by the size of the finite element and therefore a significant reduction in the size of the model can be achieved. It is assumed that at the collocation points selected, the mass and energy balances are satisfied exactly. Therefore, a more compact representation of the column module can be achieved without compromising the level of details in the description of the occurring phenomena.
The basic assumptions made for the derivation of the steady-state mass and energy balances are: (i) one-dimensional mass and heat transfer along the finite element (ii) thermodynamic equilibrium holds between the liquid and vapor phases, (iii) negligible pressure drop along the columns, (iv) solvent in the vapor phase is fully recovered due to condensation of the gas effluent stream.
The component molar flows and the stream molar enthalpy rates for both liquid and gas phase are approximated using Largrange interpolating polynomials, W. The molar and stream enthalpy flows expressed as functions of the position coordinate s, are:

$$\tilde{L}_i(s) = \sum_{j=0}^{n} W_j^L(s) L_i(s_j) \quad i = 1,....., NC, \quad j = 0,......, n \tag{1}$$

$$\tilde{V}_i(s) = \sum_{j=1}^{n+1} W_j^V(s) V_i(s_j) \quad i = 1,....., NC, \quad j = 1,......, n+1 \tag{2}$$

$$\tilde{H}^L(s) = \sum_{j=0}^{n} W_j^L(s) H^L(s_j) \qquad j = 0,......, n \tag{3}$$

$$\tilde{H}^V(s) = \sum_{j=1}^{n+1} W_j^V(s) H^V(s_j) \qquad j = 1,......, n+1 \tag{4}$$

where the Lagrange polynomials:

$$W_j^L(s) = \prod_{k=0, k\neq j}^{n} \frac{s - s_k}{s_j - s_k}, \quad j = 0,...., n \tag{5}$$

$$W_j^V(s) = \prod_{k=1, k\neq j}^{n+1} \frac{s - s_k}{s_j - s_k}, j = 1,...., n+1 \tag{6}$$

Symbols L and V in the equations denote the liquid and vapor phase respectively, whereas n is the number of collocation points in the element. Therefore, the mass balances at the collocation points take the form:

$$0 = \tilde{L}_i(s_j - 1) - \tilde{L}_i(s_j) + \tilde{V}_i(s_j + 1) - \tilde{V}_i(s_j) \quad i = 1,\ldots, NC, \quad j = 1,\ldots, n \tag{7}$$

whereas energy balance is given by:

$$\begin{aligned} 0 = &\sum_{i=1}^{NC}\left(\tilde{L}_i(s_j - 1)\right)\tilde{H}^L(s_j - 1) + \sum_{i=1}^{NC}\left(\tilde{V}_i(s_j + 1)\right)\tilde{H}^V(s_j + 1) \\ &- \sum_{i=1}^{NC}\left(\tilde{L}_i(s_j)\right)\tilde{H}^L(s_j) - \sum_{i=1}^{NC}\left(\tilde{V}_i(s_j)\right)\tilde{H}^V(s_j) - Q(s_j) \quad i = 1,\ldots, NC \qquad j = 1,\ldots, n \end{aligned} \tag{8}$$

Symbol $Q(s_j)$ denotes the heat exchanged with the environment.

Equilibrium data for CO_2 were taken using the SAFT-VR equation of state that relates CO_2 loading expressed as moles of CO_2 per mole amine to the CO_2 partial pressure. SAFT-VR implements an implicit scheme for the occurring chemical bonding of CO_2 molecules to the amine and was successfully implemented by Mac Dowell et al., 2010. Later, Rodriguez et al., 2012 extended the data to other amine-based solvents. Apart from the column section that forms the process structural block, heat exchange tasks between process streams are described by a heat transfer block without phase change tasks whereas stream mixing tasks are described by suitable mixing blocks. Another process task that is important for the representation of the process flowsheet is stream splitting as it allows connectivity of streams to multiple process units. In such blocks, the determination of the split ratios is a design variable for the system.

3. Design framework

The column section, as shown in Figure 1, is then used as the fundamental building block of a separation column, whether it performs absorption or distillation task and independent of the packing material. Therefore, a separation column may be comprised of multiple adjustable in separation capability and functionality column sections depending on the number of feed and draw streams. Column section size in terms of the position coordinate *s* indicates the number of theoretical column stages in that segment of the column. Column sections may be connected to other process blocks for the performance of the desired tasks. The ability of the column sections to interact with multiple other blocks is facilitated through the introduction of stream mixers and splitters to the liquid and vapor streams entering or leaving the column section, respectively (Figure 1). Therefore, multiple side feed streams and product streams can be accommodated within the column configuration. Overall, the selected column structure with the adjustable column sections and the connectivity possibilities provides sufficient flexibility in the generation of alternative process flowsheets. In the case of distillation/stripping columns, the associated condenser and reboiler are represented as discrete column sections of a single theoretical stage with heat exchange. The condenser and reboiler are then connected to the top and bottom column sections, respectively. The modeling equations for such blocks involve equilibrium-based material and energy balances. The overall connectivity options along with the diverse functionality of the associated blocks are shown in Figure 2.
The design variables in the flowsheet are hence the size of each column section, the heat exchanger area, the split ratios in each splitter and the column operating conditions (i.e. column pressure, reboiler and condenser duties). Obviously, the available design space can be reduced considerable by utilizing engineering practice and knowledge as well as thermodynamic and equipment constraints for the CO_2 capture system under consideration. Furthermore, sensible bounds on the design variables assist in the identification of reasonable and realizable process design solutions.
The objective function is comprised of a sum of normalized quantities aiming to the minimization of the process capital and operating costs while achieving the maximum attainable CO_2 separation. The normalization allows an easy comparison among various design alternatives and helps in balancing the different objective function goals. The objective function has the form:

$$F = \sum\frac{Q_b}{Q_b^{nom}} + \frac{a_l}{a_l^{nom}} - \frac{a_r}{a_r^{nom}} + \sum\frac{H_c}{H_c^{nom}} + \sum\frac{T_b}{T_b^{nom}} - \frac{y_{CO_2}^{in,abs} - y_{CO_2}^{out,abs}}{y_{CO_2}^{in,abs}} \tag{9}$$

Symbol Q_b is the total heat duty of all available reboilers, whereas a_l and a_r are the lean and rich solvent stream loadings, respectively. Symbol H_c is the packing height of each column calculated as the sum of the lengths L of the column sections that represent a specific column adjusted accordingly based on the packing material that is selected. Symbol T_b is the reboiler temperature, which is used in order to characterize the quality of the heat requirement for the solvent regeneration. The last term expresses the fraction of CO_2 absorbed in the process. Superscript *nom* indicates nominal values derived for the base design case from which an improvement is sought.

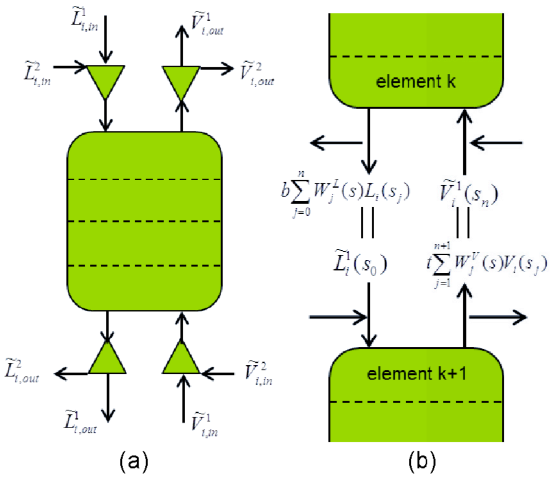

Figure 1: (a) Column section with mixing and splitting tasks, (b) Column sections connectivity.

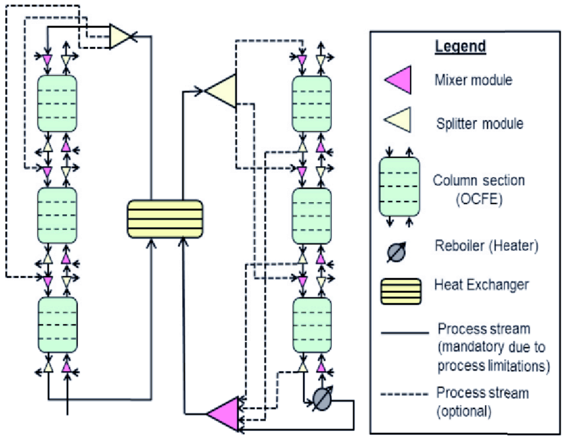

Figure 2: Process flowsheet connectivity and functionality.

4. Case study results

The optimal design of an efficient MEA (monoethanolamine) based CO_2 capture process flowsheet is performed. The inlet stream data and imposed process constraints are summarized in Table 1. Four different flowsheet configurations as shown in Figure 3 have been identified as potentially good candidates for a highly performing solution. Design flowsheet A represents the conventional process configuration that has been exhaustively investigated. Design flowsheet B distributes the thermal duty along the stripper through the introduction of a second reboiler and a side feed stream. The main aim in this design is an efficient separation by imposing a uniform driving force in the stripping column. Design flowsheet C attempts to distribute the rich solvent stream along the stripper with multiple feeding points. Finally, design flowsheet D aims at a more uniform concentration gradient and therefore a higher average driving force for the separation along the reactive absorption unit through the implementation of a side feed stream.

The design optimization results for the four flowsheets are presented in Table 2. The nonlinear program has been solved using MINOS 5.5 that employs an augmented Lagrangian reduced gradient algorithm (Murtagh and Saunders, 1998). Design flowsheet A resulted in the worst value for the objective value. The large values of the heat exchanger area combined and the elevated temperature in the stripping column reboiler have the greatest impact on the objective function value. Regarding the operating conditions flowsheet A uses the largest pressure in the stripping column among all design options. Is should be noted that compression costs are not considered in the objective function as the higher pressure in the stripper will be balanced with a lower compression load for the CO_2 product stream. The elevated pressure assists the desorption of the gas from the solvent but leads to higher reboiler temperature but lower heat duty. This trend is clearly obtained by the inspection of the optimization results. Flowsheet design C results in the lowest objective function value among all design alternatives but quite close to the corresponding value for flowsheet design B. In both of design options B and C, CO_2 absorption fraction has reached a value of 99.98 % much higher than the imposed specification.

The distribution of the rich CO_2 solvent stream liquid stream through multiple feed points in the stripping column tends to regulate the temperature profile of the column in a way such that average distillation driving forces are kept at a high level hence increasing the separation efficiency. The low heat duty in the reboilers, and the low operating pressure in the strippers demonstrate the higher efficiency of the selected column configuration. Also, flowsheet designs B and C exhibit heat exchanger areas that are smaller than those obtained by flowsheets designs A and D. An interesting observation is the achievement of low loadings in the lean stream and higher loadings in the rich stream compared to the other two options. Finally, flowsheet design D appears to results in improved performance compared to flowsheet design A. The multiple feedings points of the lean solvent in the absorber clearly enhance column efficiency with a higher loading in the rich stream but result in a drastic increase of the absorption column size (e.g. from 12 theoretical stages in design A to 30 theoretical stages in design D).

Table 1: Base case values used in the optimal design optimization

Solvent (amine)	MEA
Fresh solvent concentration (% wt)	30
Solvent flow in absorber (mol/s)	16.3965
Minimum lean solvent loading	0.23
Inlet gas flow in absorber (mol/s)	6.0033
Inlet gas composition (mol/mol): $H_2O/CO_2/N_2$	0/0.09041/0.90959
Inlet gas temperature in absorber (K)	298.15
Maximum liquid inlet temperature in absorber (K)	313
Minimum CO_2 absorption (%)	98

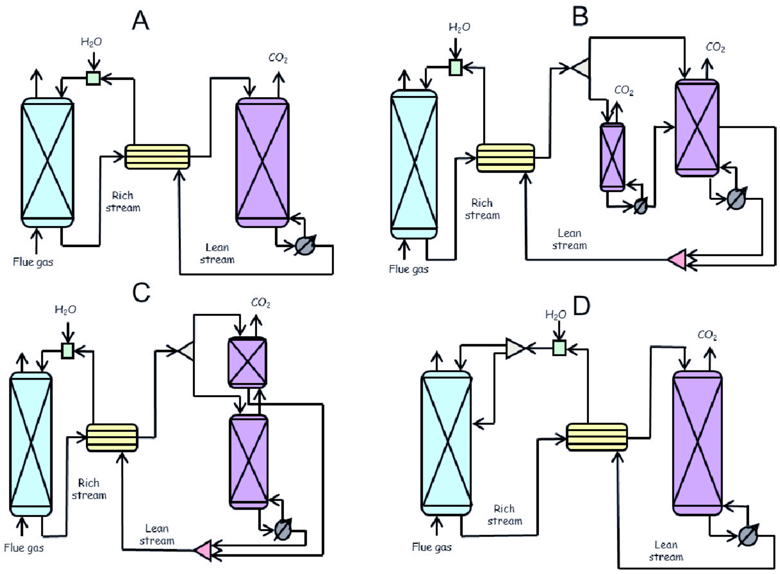

Figure 3. Alternative flowsheets used in the design optimization.

Table 2: Design optimization results

	A	B	C	D
CO_2 absorption (%)	98	99.98	99.98	98
Lean loading	0.2458	0.2394	0.2394	0.2657
Rich loading	0.456	0.5425	0.5424	0.4898
Side-draw loading	-	0.4216	0.4711	-
Stages: Absorber/Stripper (main)/Stripper (2^{nd})	13/26/-	12/30/3	12/28/3	30/38/-
Reboiler (main)/ 2^{nd} duty (kW)	42.535	45.364/1.782	47.058	38.227
Reboiler (main) temperature (K)	396.62	376.78	376.72	386.72
Liquid inlet temperature in absorber (K)	313	313	313	313
Heat exchanger area (m^2)	86.36	65.62	65.42	79.36
Pressure in stripper (kPa): main / 2^{nd}	201.5/-	101.3/101.3	101.3/101.3	146.98/-
Split ratio (%)	-	20.40	9.051	44.77
Side split ratio (%)	-	17.062	-	-
Objective function value	1.94902	1.59161	1.57952	1.66932

Conclusions

In the present work, a framework for the design of solvent-based CO_2 separation processes via reactive absorption and solvent recovery is developed. The process flowsheet is decomposed into fundamental structural blocks that perform specific tasks. Column sections are the fundamental block for the separation columns that employs equilibrium-based process models that become compact in size through the implementation of an OCFE formulation. OCFE formulation through a suitable selection of finite elements and collocation points per element ensures high accuracy within a flexible modeling context. Connectivity among the building blocks is achieved through a set of mixers and splitters attached to the streams associated with the column section blocks. The proposed framework was used for the optimal design of four alterative process flowsheets for the capture of CO_2 from a flue gas stream using an aqueous MEA solution. Optimization results showed that the efficiency of the process can be significantly improved with a targeted assessment of alternative design options. Obviously, the design framework can be further extended to other solvent mixtures for a definite evaluation of solvent-process options.

Acknowledgements

The authors would like to thank Prof. Claire Adjiman, Dr. Alexandros Chremos, Prof. Amparo Galindo, and Prof. George Jackson of Imperial College London for providing the SAFT-VR thermodynamic models.
The financial support of the European Commission through project FP7-ENERGY-2011-282789 is gratefully ackowledged.

References

Cousins, A., Wardhaugh L.T., Feron, P.H.M., 2011, A survey of process flow sheet modifications for energy efficient CO_2 capture from flue gases using chemical absorption, International Journal Greenhouse Gas Control, 5, 605-619.

Ismail. S.R., Proios, P., Pistikopoulos, E.N., 2001, Modular synthesis framework for combined separation/reaction systems, AIChE J., 47, 629-649.

Jassim, M.S., Rochelle, G.T., 2006, Innovative absorber/stripper configurations for CO_2 capture by aqueous monoethanolamine, Industrial and Engineering Chemistry Research, 45, 2465-2472.

Kenig, E., Seferlis, P., 2009, Modeling reactive absorption, Chemical Engineering Progress, January, 65-73.

Le Moullec, Y., Kanniche, M., 2010, Description and evaluation of flowsheet modifications and their interaction for an efficient monoethanolamine based post-combustion CO_2 capture, Chemical Engineering Transactions, 21, 175-180.

Mac Dowell, N., Llovell, F., Adjiman, C.S., Jackson, G., Galindo, A., 2010, Modeling the fluid phase behavior of carbon dioxide in aqueous solutions of monoethanolamine using transferable parameters with the SAFT-VR approach, Industrial and Engineering Chemistry Research, 49, 1883-1899.

Moioli, S., Pellegrini L.A., 2013, Regenaration section of CO2 capture plant be MEA scrubbing with a rate-based model, Chemical Engineering Transactions, 32, 1849.

Murtagh, B.A. and Saunders, M.A., 1998 MINOS 5.5 User's Guide. Technical Report SOL 83-20R, Stanford University, USA.

Oyenekan, B.A. 2007, Modeling of strippers for CO_2 capture by aqueous amines, PhD Thesis, University of Texas at Austin, USA.

Proios, P., Pistikopoulos, E.N., 2006, Hybrid generalized modular/collocation framework for distillation column synthesis, AIChE J., 52, 1038-1056.

Rodriguez, J. Mac Dowell, N. Llovell, F., Adjiman, C.S., Jackson, G., Galindo, A., 2012, Modeling the fluid phase behaviour of aqueous mixtures of multifunctional alkanolamines and carbon dioxide using transferable parameters with the SAFT-VR approach, Molecular Physics, 110, 11-12.