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A structured approach for selecting carbon capture process models. A case study on monoethanolamine

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Abstract

Carbon capture and storage is considered a promising option to mitigate CO_2 emissions. This has resulted in many R&D efforts focusing at developing viable carbon capture technologies. During carbon capture technology development, process modeling plays an important role. Selecting an appropriate process model for carbon capture technologies is not trivial, because of the large range of technology options, the difference in technology development stage, and the different purposes for which a process model can be used. This paper proposes a five-step, structured approach, designed to support the selection of carbon capture process models. The approach is illustrated with a post-combustion (monoethanolamine) case study. The paper shows intermediate and output results of the structured approach, and of the MEA case.

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Keywords: Process modeling; model selection; carbon capture; MEA; structured approach; attribute complexity matrix.

1. Introduction

Carbon capture and storage is generally considered a promising option to mitigate anthropogenic CO_2 Emissions. For this reason, many R&D efforts focus at developing viable carbon capture technologies. Some of these technologies are well-established, many are relatively new. During Research and Development, modelling of carbon capture technologies plays an important role. Process models are used to assess performance, optimize processes or to serve as input for further analysis (economic, environmental).

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Process model selection is an important step, because it determines, to a large extent, the quality of the model results. Selection is highly dependent on the type of technology that is modeled, and on the objectives that the model is supposed to fulfill. As an example, figure 1 shows a (non-exhaustive) number of carbon capture technologies that is currently under development. They are grouped into type (post-combustion, pre-combustion, and oxyfuel) and by Technology Readiness Level[2]. For technologies at a very early stage of development (low TRL), little data is available, limiting the type of process models that can be specified. For mature technologies (high TRL), there is often a range of possible models to choose from. Different technology types, e.g. solvent, PSA, or oxyfuel plants, require different kinds of models. The same applies to the modeling objective. If a model is to supply a detailed output for a LCA study, a different model will be chosen than when the aim is to perform a quick scan of technology performance.

To support the model selection process for carbon capture technologies, we suggest a structured approach consisting of five steps. This approach has been developed as part of a larger study that focuses on selection and quality evaluation of process models, economic models, and LCA models [1]. In future work, the structured approach for process model selection will be complemented with an approach for process model evaluation.

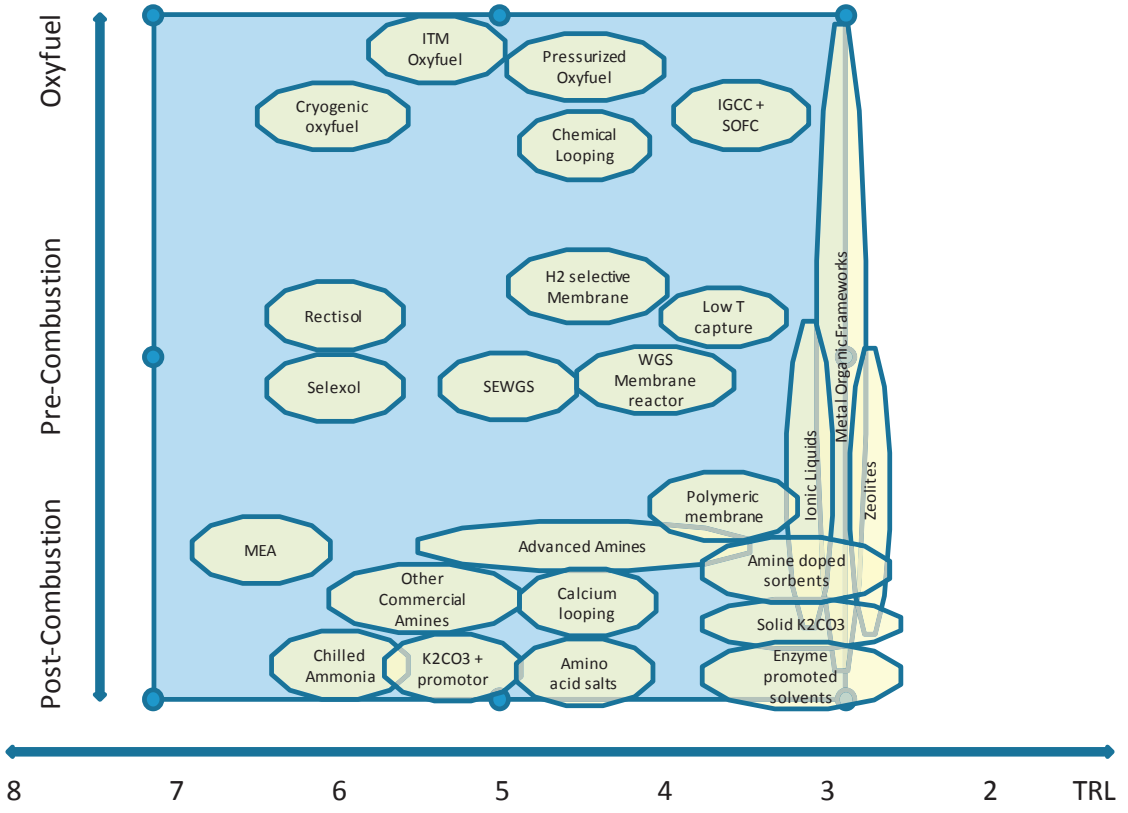

Figure 1.Selection of carbon capture technologies, clustered by type, and Technology Readiness Level

[2] Technology Readiness Level (TRL) is a measure for the maturity of a technology. It uses a scale that runs from 1 to 9, where a figure of 1 represents technology that is at a very early stage of research, and a figure of 9 represents technology that is operating in a commercial environment over the entire range of conditions it was designed for. The TRL scale was first developed by NASA for use in their space programmes, and later adapted for energy technologies by the US Department of Energy [27].

2. Approach

In order to gain deeper understanding of process model selection, discussions were organized with several modeling experts from academia, research institutes, and corporations. Initial discussions where on a one to one basis, using a semi-structured interview format. At a later stage, follow-up discussions took place in a Group Decision Room, an environment that enables group brainstorming and group decision-making, using hardware (computer for each individual participant connected to a network system), software (to allow brainstorming, ranking and structuring of ideas), and process facilitation [2]. One of the results of the interviews and workshop was that model selection follows a sequence of iterative steps. When the experts were asked which steps they take during model selection, the following five were mentioned most often:

1) Understand the process
2) Define modeling objective
3) Specify selection criteria
4) Select model attributes
5) Specify and run the model

We include these five steps as the basis of the approach. The following section further illustrates each step, using an evaluation of a power plant with monoethanolamine CO2 capture, which was done as case study for the Eddiccut project [3].

3. Illustration of the approach with MEA post combustion solvent example

3.1. Understand the process

"So you start with trying to understand the process itself, that is the first step". Senior Scientist gas treatment, TNO (Netherlands Organization for Applied Scientific Research)

The first step of the approach, aims to gain understanding of the process. It is important to understand the current knowledge on the capture process, in order to pick the suitable model in a later step. For the purpose of process simulation, the following aspects are interesting to study, as they form the basic elements of a model : components and their properties, chemistry, thermodynamics and process line-ups.

For the MEA case, step 1 led to the following understanding: the main components in a MEA solvent are MEA, water, CO_2 and their solutes ($MEAH^+$, $MEACOO^-$, CO_3^{2-}, HCO_3^-, OH^-, H_3O^+). Flue gas typically consists of Nitrogen, Oxygen, water and CO_2. Besides that, flue gas can contain many impurities like SO_x, NO_x, particulates, halogen compounds and heavy metals [4]. For the main substances, pure component data is available through software databanks, amongst others [5]. MEA-H_2O-CO_2 chemistry can be described by relations using the minimization of Gibbs free energy [6], equilibrium constants [7], and power law kinetics [8]. Good quality data on the chemistry is available in literature and in software databanks. In the solvent, also side and impurity reactions take place, producing heat stable salts and other degradation products. These reactions and reaction products have been studied, but the level of understanding is not as high as for the main reactions. For instance, reaction mechanisms have been proposed, and degradation rates are measured, but the results are still partial in nature, and are not combined yet into integrated degradation chemistry and kinetics, see e.g. [9]–[11]. Thermodynamics describing MEA-H_2O-CO_2 heat of absorption, phase equilibria, and speciation, have been described in many studies, e.g. [6], [7], [12]–[14]. Some studies propose simplified thermodynamic relations, others define complex, rigorous relations, including activity coefficient models. With respect to line-ups, the standard line-up for a MEA system includes a simple absorber stripper system with cross heat exchanger. Both absorber and stripper are typically equipped with a water wash to prevent MEA loss [15]. More advanced configurations have been proposed, containing energy integration methods to reduce the energy penalty for capture, e.g. [16]. Commercial vendors, like Fluor and Aker, have their own process line-ups, but the exact flowsheets are proprietary and not publicly available [17].

3.2. Define modeling objective

"The thing I always stress the most is that the purpose must be clear. You have to be able to formulate,…, as detailed as you can, the reason why you are developing this model". Professor modeling and simulation of process and energy stystem, Delft University of Technology.

A modeling objective describes the purpose of the model and its results, and describes what questions the model is required to answer [18]. The modeling objective can be specified based on the information gathered in step 1, on the broader research context in which the modeling study is pursued, and on the requirements of possible clients. Defining a good modeling objective is important, because it gives direction to selection of the process model in later steps. The modeling objective should be clear and concise. For the MEA case, the modeling objective was *to assess the technical performance of a MEA carbon capture unit connected to a pulverized coal power plant as a benchmark for novel carbon capture technologies*.

3.3. Specify selection criteria

"In the beginning of the project, this was very important, and I would advise you to do it, we wrote a document where we outlined all the criteria". Professor modeling and simulation of process and energy systems, Delft University of Technology.

By defining the modeling objective, direction is given to the selection of the process model. Selection criteria can be defined to further reduce the selection space, i.e., criteria that can limit the amount of models to choose from. Model selection criteria that are found in literature most frequently include reliability, time availability, accuracy, predictability and data availability [14], [18]–[24]. During the expert sessions described in section 2, we asked which selection criteria participants use in their modeling. This revealed the following additional criteria: availability of in-house knowledge, client expectations, required output indicators, and required level of detail, amongst others.

For the MEA case, the following criteria were specified:

1) *Time*: the model should be selected, specified and run in two months.
2) *Accuracy*: the model should be accurate enough to serve as a benchmark for other carbon capture technologies.
3) *Parameter availability*: the model should run on existing physical property data.
4) *Level of detail*: the level of output detail should be high enough to serve as input for rigorous economic analysis.

3.4. Select model attributes

"Complexity is important, because you can easily try and make a model too complex, unnecessarily. The choice for complexity depends on how well you know the process you are modeling". Senior scientist, European energy utility company.

Rather than choosing a process model as a whole, we suggest to break down the model into its attributes, as this makes the selection easier, more formalized, and more informed. The model attributes are defined along five dimensions (inputs & outputs, chemistry & conversion, thermodynamics, building blocks, and process integration) and five levels of complexity (from very low to very high), together forming an attribute complexity matrix (figure 2). *Inputs and outputs* are defined as the components that flow into and out of the model. They may contain the main components, impurities, utility streams, and process chemicals. *Chemistry and conversion* deals with how complex one decides to model the chemical reactions in the model. A choice can be made for specifying simple yields, or including equilibrium or power law kinetics. In this dimension it can also be specified if mass and heat transfer are

included, and if only the main reactions are taken into account, or also side reactions. The *Thermodynamics* dimension defines what kind of thermodynamic and phase equilibria models are used. This ranges from very simple heat balances and ideal thermodynamics to rigorous thermodynamics, including Equations of State and activity coefficient models. Using the dimension *building blocks*, one can specify the detail of the flowsheet (only the main blocks vs. all equipment) and the level of detail of the individual blocks (e.g. simple heat exchanger vs. rigorous heat exchanger). The last dimension, *process integration*, is used to select the level of integration in the flowsheet: are recycle loops included, is there heat integration and how much, or is a fully optimized flowsheet required?

Figure 2 shows the choices made for the MEA case. In this case it was chosen to only model the main components (N_2, H_2O, CO_2, MEA) and their solutes in the flue gas and aqueous MEA solvent, and only take into account the most common other substances in the flue gas (Ar and O_2). Given the modeling objective and criteria, it was not required to include other impurities, or solvent degradation products. Secondly, it was chosen to model the chemistry using equilibrium coefficients, because these coefficients are readily available in literature, and supply sufficiently accurate results. In particular, we selected the coefficients from Kim et al. [7], because these coefficients were well validated. In addition to that, mass transfer limitations were used in the columns to increase the accuracy of the model. Thirdly, it was chosen to describe thermodynamics by the rigorous e-NRTL-RK model, to fulfill the criterion of accuracy. More specific, to also fulfill the criteria of time and parameter availability, the VLE model and parameters are used as available in the Aspen Plus databanks [5]. The Aspen databank parameters were used instead of regressing parameters from experimental data ourselves, because the latter would require much more time than the available two months (criterion 1).

Complexity Level	Inputs & Outputs	Chemistry &Conversion	Thermodynamics	Building blocks	Process integration
5. Very high	All components, impurities, utilities and process chemicals	Detailed kinetics including heat/mass transfer limitations, side reactions and impurity reactions	Rigorous thermodynamic models	Optimized equipment specification including temperature and pressure changers	Detailed process optimization against predefined criteria
4. High	All components, impurities, utilities and process chemicals	Detailed kinetics including heat/mass transfer limitations, side reactions and impurity reactions	Rigorous thermodynamic models	Detailed equipment specification including temperature and pressure changers	Detailed heat & mass integration
3. Average	Main components and main impurities	Basic chemistry included, modeled following thermodynamic equilibrium	Intermediate complexity thermodynamic models	Simple equipment specification including temperature and pressure changers	Main heat and mass integration included
2. Low	Main components	Theoretical yield/conversion specified	Short-cut thermodynamic models	Main building blocks represented as black boxes	Basic recycle loops included
1. Very low	Main components	Not specified	Simple heat balance, ideal thermodynamics	Not Specified, whole process is one black box	Not specified

Figure 2. Attribute complexity matrix for the MEA model.

To be able to supply a detailed equipment list (criterion 4), we chose to include all heat exchangers and pumps, including the ones of the DCC and water wash recycle streams (figure 3). Some models only include the major pumps (e.g. absorber bottom pump), but that would render too little detail for cost estimation. Most of the pumps and HX's were modelled using simple unit operation models. Only the cross heat exchanger and the columns were

modelled using more detailed unit operation models, enabling rate based chemistry in the columns and realistic heat flux in the cross-HX.

The process in figure 3 resembles a basic solvent process for flue gas carbon capture. It is possible to increase complexity of the flowsheet, e.g. by adding more advanced energy integration options. However, because the modeling objective was to generate a *benchmark* for other carbon capture technologies, we chose not to do this. Adding more complexity to the flowsheet would stray from modeling a generic benchmark, or base case, and would rather move towards modeling a specific vendor's technology.

Summarizing, most model attributes were selected at an average to high level of complexity (grey shading in figure 2). The matrix provided a clear choice of attributes that aids in defining the process model. As such, the matrix can be a useful tool for selecting the right MEA model for the given objective, and helps minimize under or overspecification.

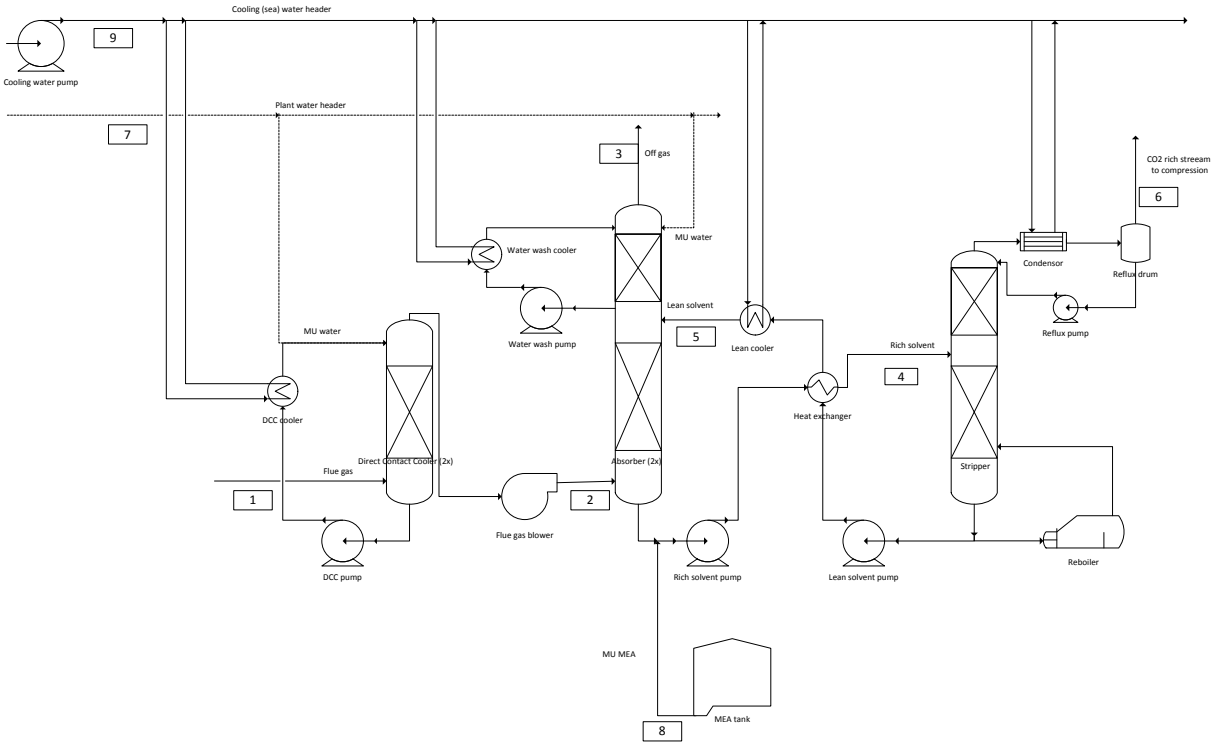

Figure 3. Process Flow Diagram of the MEA model.

In conjunction with selection of attributes, the software is selected. As we use the e-NRTL-RK thermodynamic coefficients from the Aspen Plus databanks, we chose to use this software. Another, but secondary reason to work with this software, was because of available in-house knowledge of Aspen Plus simulation.

3.5. Specify and run model

In the last step of the approach, the process model is specified in the chosen software. We specified the MEA model according to the attribute selections made in step four, i.e. using the flowsheet in figure 3, the thermodynamics from the Aspen Plus databanks, and the chemistry and equilibrium coefficients as proposed by Kim et al [7].

3.6. Model results

Table 1, shows the results of our MEA model and compares those to results as found in the Esbjerg pilot plant [15], [25], [26]. As can be seen, the results agree fairly well with the validation plant.

Table 1. Results of the MEA model (this work), and validation against the Esbjerg pilot plant data.

	This study	**Validation**
Specific Reboiler Duty (GJ/t CO_2)	3.6	Esbjerg: 3.6-3.9
Liquid/gas ratio ($kg_{solvent}/kg_{flue\ gas}$)	3.8	Esbjerg: 3-3.5
Electric power requirement (MJ/t CO_2)	122.3	-
Cooling water requirement (GJ/t CO_2)	4.1	Esbjerg: 3.2-3.9
Plant water requirement (m^3/t CO_2)	0.53	-
CO_2 in stripper overhead (%)	95.9	Esbjerg: 96.9

4. Conclusions and further work

In this paper, we presented a five-step approach for carbon capture model selection, and illustrated the approach on a MEA post combustion case study. The approach supports the model selection process, and can aid in making informed and explicit decisions on model selection. At the core of the approach is the use of an attribute complexity matrix. Further research is currently being carried out to extend the approach with model quality evaluation tools, in order to assess quality of the model and integrate this information in the assessment of results, and to communicate the quality of modeling study outputs to decision makers. This integrated approach for model selection and model quality evaluation will be further tested on a number of carbon capture and carbon utilization case studies. This is subject to research that will be pursued in the Eddiccut project in the period 2014 - 2017.

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References:

[1] B. Singh, M. W. Van der Spek, W. B. Schakel, R. Skagestad, H. A. Haugen, A. Ramirez, N. H. Eldrup, E. G. Hertwich, and A. H. Strømman, “Environmental Due Diligence of CO2 Capture and Utilization Technologies - Framework and Application,” *Energy Procedia*.

[2] A. Ramírez, M. Hoogwijk, C. Hendriks, and A. Faaij, “Using a participatory approach to develop a sustainability framework for carbon capture and storage systems in The Netherlands,” *Int. J. Greenh. Gas Control*, vol. 2, no. 1, pp. 136–154, Jan. 2008.

[3] “Eddiccut.” [Online]. Available: www.eddiccut.com.

[4] E. Sanchez Fernandez, E. Goetheer, M. Juzwicka, T. Van Harmelen, and A. Van Horssen, “Emissions of substances other than CO2 from power plants with CCS, 2012/03,” Stoke Orchard, 2012.

[5] Aspentech, “Aspen Plus.” Aspentech, Ten Canal Park, Cambridge, Massachusetts, 02141-2201, US, 2014.

[6] Y. Zhang, H. Que, and C.-C. Chen, “Thermodynamic modeling for CO2 absorption in aqueous MEA solution with electrolyte NRTL model,” *Fluid Phase Equilib.*, vol. 311, pp. 67–75, Dec. 2011.

[7] I. Kim, K. a. Hoff, E. T. Hessen, T. Haug-Warberg, and H. F. Svendsen, "Enthalpy of absorption of CO2 with alkanolamine solutions predicted from reaction equilibrium constants," *Chem. Eng. Sci.*, vol. 64, no. 9, pp. 2027–2038, May 2009.

[8] H. M. Kvamsdal and G. T. Rochelle, "Effects of the Temperature Bulge in CO 2 Absorption from Flue Gas by Aqueous Monoethanolamine," *Ind. Eng. Chem. Res.*, vol. 47, pp. 867–875, 2008.

[9] C. Gouedard, D. Picq, F. Launay, and P.-L. Carrette, "Amine degradation in CO2 capture. I. A review," *Int. J. Greenh. Gas Control*, vol. 10, pp. 244–270, Sep. 2012.

[10] T. Supap, R. Idem, P. Tontiwachwuthikul, and C. Saiwan, "Kinetics of sulfur dioxide- and oxygen-induced degradation of aqueous monoethanolamine solution during CO2 absorption from power plant flue gas streams," *Int. J. Greenh. Gas Control*, vol. 3, no. 2, pp. 133–142, Mar. 2009.

[11] A. J. Sexton and G. T. Rochelle, "Reaction Products from the Oxidative Degradation of Monoethanolamine," *Ind. Eng. Chem. Res.*, vol. 50, no. 2, pp. 667–673, Jan. 2011.

[12] A. Tobiesen and H. Schumann-Olsen, "Obtaining optimum operation of CO2 absorption plants," *Energy Procedia*, vol. 4, pp. 1745–1752, Jan. 2011.

[13] E. T. Hessen, T. Haug-warberg, and H. F. Svendsen, "The refined e-NRTL model applied to CO2–H2O–alkanolamine systems," *Chem. Eng. Sci.*, vol. 65, no. 11, pp. 3638–3648, 2010.

[14] R. Notz, I. Tönnies, H. P. Mangalapally, S. Hoch, and H. Hasse, "A short-cut method for assessing absorbents for post-combustion carbon dioxide capture," *Int. J. Greenh. Gas Control*, vol. 5, no. 3, pp. 413–421, May 2011.

[15] J. N. Knudsen, J. Andersen, J. N. Jensen, and O. Biede, "Evaluation of process upgrades and novel solvents for the post combustion CO2 capture process in pilot-scale," *Energy Procedia*, vol. 4, pp. 1558–1565, Jan. 2011.

[16] H. Ahn, M. Luberti, Z. Liu, and S. Brandani, "Process configuration studies of the amine capture process for coal-fired power plants," *Int. J. Greenh. Gas Control*, vol. 16, pp. 29–40, Aug. 2013.

[17] E. S. Rubin, H. Mantripragada, A. Marks, P. Versteeg, and J. Kitchin, "The outlook for improved carbon capture technology," *Prog. Energy Combust. Sci.*, vol. 38, no. 5, pp. 630–671, Oct. 2012.

[18] R. Gani and J. P. O'Connell, "A knowledge based system for the selection of thermodynamic models," *Comput. Chem. Eng.*, vol. 13, no. 4, pp. 397–404, 1989.

[19] P. J. T. Verheijen, "Model Selection : an overview of practices in chemical engineering," *Comput. Chem. Eng.*, vol. 16, no. 16, pp. 85–104, 2003.

[20] Z. Švandová, J. Labovský, J. Markoš, and Ľ. Jelemenský, "Impact of mathematical model selection on prediction of steady state and dynamic behaviour of a reactive distillation column," *Comput. Chem. Eng.*, vol. 33, no. 3, pp. 788–793, Mar. 2009.

[21] E. Y. Kenig, R. Schneider, and A. Go, "Reactive absorption : Optimal process design via optimal modelling," *Chem. Eng. Sci.*, vol. 56, pp. 343–350, 2001.

[22] M. T. Ho, G. W. Allinson, and D. E. Wiley, "Reducing the Cost of CO 2 Capture from Flue Gases Using Pressure Swing Adsorption," *Ind. Eng. Chem. Res.*, vol. 47, pp. 4883–4890, 2008.

[23] M. Wang, a. Lawal, P. Stephenson, J. Sidders, and C. Ramshaw, "Post-combustion CO2 capture with chemical absorption: A state-of-the-art review," *Chem. Eng. Res. Des.*, vol. 89, no. 9, pp. 1609–1624, Sep. 2011.

[24] A. B. Rao and E. S. Rubin, "A technical, economic, and environmental assessment of amine-based CO2 capture technology for power plant greenhouse gas control.," *Environ. Sci. Technol.*, vol. 36, no. 20, pp. 4467–75, Oct. 2002.

[25] J. N. Knudsen, J. N. Jensen, and P. Vilhelmsen, "First year operation experience with a 1 t / h CO 2 absorption pilot plant at Esbjerg coal-fired power plant," in *Proceeedings of European Congress of Chemical Engineering*, 2007, no. September, pp. 16–20.

[26] F. Ahmadi, "ASSESSING THE PERFORMANCE OF ASPEN PLUS AND PROMAX FOR THE SIMULATION OF CO 2 CAPTURE PLANTS," University of Regina, 2012.

[27] US Department of Energy, "U . S . DEPARTMENT OF ENERGY Technology Readiness Assessment Guide," 2009.