Dynamic Data Reconciliation and Model Validation of a MEA-Based CO2 Capture System using Pilot Plant Data

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This work focuses on development of a “gold standard” process model for a MEA-based post-combustion CO2 capture process. The steady-state model includes a comprehensive thermodynamic framework in conjunction with the chemistry model. Parameters for all thermodynamic, transport, and physical properties models are regressed using extensive data available in the literature. An integrated mass transfer model is developed and validated using experimental data. The steady-state model is validated using data collected from the U.S. DOE’s National Carbon Capture Center (NCCC) in Wilsonville, Alabama. In addition to the steady-state runs, dynamic test runs were conducted at NCCC by introducing carefully-designed step changes and recording the transients of all key variables. Due to measurement noise and missing measurements for a number of key variables, a dynamic data reconciliation problem was solved to ensure material and energy balance of the collected data. Both the steady-state and dynamic models were validated against plant data for a wide range of operating conditions.

Keywords: Dynamic modeling, validation, dynamic data reconciliation, MEA solvent modeling, CO2 capture

1. INTRODUCTION

Due to growing concern over increases in CO2 concentration in the environment, a number of options are being investigated. Post-combustion CO2 capture is one of the key technologies that can have a strong effect on the CO2 inventory in the air. In order to be commercially successful, these technologies should not only be economically viable, but also need to be operable and controllable when coupled to a power plant. High-fidelity process models are invaluable in studying the dynamic behavior of these processes in the face of disturbances and setpoint changes. Development of such rigorous and robust process models is one of the focus areas of the United States Department of Energy’s Carbon Capture Simulation Initiative (CCSI) (Miller et al. 2014). CCSI is a partnership among national laboratories, industry, and academic institutions that is developing, demonstrating, and deploying state-of-the-art computational tools and models to accelerate the development, scale up, and commercialization of carbon capture technologies.

This work focuses on the development and validation of a “gold standard” model that will serve as a definitive reference for the aqueous monoethanolamine (MEA) solvent-based post-combustion CO2 capture system over a large operating range. Along with theoretical developments, an extensive amount of experimental data is needed for developing and validating a “gold standard” model. The MEA system has been the industry standard for solvent-based CO2 capture since 1970 (Amundsen et al. 2009) and is considered a baseline for comparison with other potential systems due to the widespread availability of substantial property and process data in the open literature.

In order to develop a “gold standard” model, several requirements must be met. All physical property models should generate satisfactory estimates over the entire range of operating conditions of the CO2 absorption and solvent regeneration processes. It is difficult to measure some of the properties, such as diffusivity, especially for chemical solvents where chemical reactions simultaneously take place along with mass transfer. For such properties, kinetic and mass transfer models should be developed simultaneously with the physical property models on which they depend, and they should also be validated with experimental data. Hydraulic models play a key role in calculating the mass and heat transfer rates as well as kinetic rates. Since MEA-CO2-H2O is a reactive system, the thermodynamic framework must be developed in conjunction with the chemistry model. The overall process model, which consists of the aforementioned submodels, needs to be validated with both steady-state and dynamic process data over the operational ranges of industrial interest.

Currently, most of the models available in the open literature for solvent-based CO2 capture systems are primarily limited to steady-state operating conditions and have been validated over a narrow range of operating conditions. Dynamic validation
for a limited range of absorber operation is given in the work of Kvamsdal et al. (2011). Dynamic data reconciliation (DDR) strategies are presented in the work of Tellez-Schmill et al. (2007) and are often useful to reduce or eliminate random or systematic measurement errors from experimental data. In this work, dynamic models are developed in leading software platforms such as Aspen Plus Dynamics® and gPROMS® and validated with dynamic data from the U.S. DOE’s National Carbon Capture Center (NCCC) pilot plant in Wilsonville, Alabama.

2. MODEL DEVELOPMENT

The steady-state MEA model is implemented in Aspen Plus®, and the absorber and stripper columns are modeled as rate-based columns. The rigorous rate-based model is used instead of the equilibrium model, which is generally inappropriate for modeling reactive distillation systems. A summary of the differences between rate-based and equilibrium column simulations is given by Taylor et al. (2003). The models required for the rate-based simulation include thermodynamic and physical property models, kinetic model(s), mass transfer models, and hydraulic models. In this work, these models are developed as individual submodels and incorporated into the overall process model.

Physical property models developed in this work include standalone models and an integrated thermodynamic framework. Standalone models for viscosity, density, and surface tension of the system have been developed, with uncertainty quantification, as described in Morgan et al. (2015). Even though this work started off with the thermodynamic model used in the Phoenix model (Plaza 2012), significant changes have been made to that model as described below. As in the Phoenix model, the solution thermodynamics in the new model are represented by the ELECNRTL method, which uses the Redlich-Kwong equation of state to calculate the vapor phase fugacity coefficients and the electrolyte non-random two liquid (e-NRTL) model to calculate the activity coefficients in the liquid phase. To ensure thermodynamic consistency in the model, multiple data types are regressed simultaneously. Approximately 500 vapor-liquid equilibria (VLE) data from various sources (Aronu et al. 2011; Dugas 2009; Hilliard 2008; Jou et al. 1995; Lee et al. 1976; Ma’mun et al. 2005; Xu 2011) for the ternary MEA-H2O-CO2 system are included, and these data span the wide temperature and composition range of interest for absorber and stripper operation. Also included in the regression are heat capacity (Weiland et al. 1997) and heat of absorption (Kim et al. 2013) data. Since heat of absorption, which was not included in the Phoenix model regression, is not calculated directly as a property in Aspen Plus®, the property is defined in a FORTRAN user model and incorporated into the Aspen Data Regression System. Binary MEA-H2O system VLE data (Cai et al. 1996; Tochigi et al. 1999) which were not considered in the Phoenix are also included in this new model. A total of eleven parameters are included in the regression, and parameter selection was performed using Akaike Information Criterion (AIC) (Akaike 1974). This allowed for the model to contain a smaller parameter space in comparison with the Phoenix model, without deterioration in the fit to the experimental data. The fit of this model compared to selected ternary VLE data and heat of absorption data is shown in Figures 1-2.

![Figure 1- Results from the thermodynamic model vs experimental ternary VLE data (30 wt% MEA)](image1)

![Figure 2 – Results from the thermodynamic model vs heat of absorption data (30 wt% MEA)](image2)

The kinetic model is based on the reactions used in the Phoenix model, in which overall ionic speciation of the system is simplified into two equilibrium reactions:

$$2\text{MEA} + \text{CO}_2 \leftrightarrow \text{MEA}^+ + \text{MEACOO}^- \quad (1)$$

$$\text{MEA} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{MEA}^+ + \text{HCO}_3^- \quad (2)$$

The forward reaction kinetics are taken from the Phoenix model. Following the methodology of Mathias and Gilmartin (2014), the reaction rates are written in terms of the reaction equilibrium constants, which are also calculated as part of the thermodynamic framework of the system.

The hydrodynamic models developed in this work include models for pressure drop and hold-up. Correlations from Stichlmair (1989) and Billet and Schultes (1999) are selected for evaluation due to their applicability over the entire range of solvent loadings of interest and include specific parameters that can be calibrated for MellapakPlus™ 252Y, the packing
used at NCCC. The correlations are regressed with the experimental data of this packing type from Tsai (2010). The final correlation selected is from Billet and Schultes (1999) due to its higher accuracy for both low (0.8 cP) and high viscosity (12 cP) cases, when compared to the predicted values from Stichlmair et al. (1989).

Typically, mass transfer models and the parameters on which they depend, including liquid and gas-side mass transfer coefficients, diffusivity, and interfacial area, are regressed using data obtained from different experimental set-ups and scales, often in a sequential manner. This sequential methodology leads to an increased parametric uncertainty that is compounded with each regression. In this work, a novel and integrated methodology to obtain the mass transfer model is proposed, so that the accuracy and reliability of the aforementioned models can be improved. In this integrated mass transfer model, parameters for the interfacial area, mass transfer coefficients, and diffusivity models are simultaneously regressed using wetted wall column data from Dugas (2009) and pilot plant data from Tobiesen et al. (2007).

This simultaneous regression of process model and property model parameters cannot be accomplished directly in the Aspen Plus® property regression system. Instead, the CCSI Framework for Optimization, Quantification of Uncertainty and Surrogates (FOQUS) provides a computational platform in which this integrated mass transfer model can be regressed using a derivative-free optimization (DFO) algorithm.

The aforementioned submodels are integrated into steady-state and dynamic process models in Aspen Plus® and Aspen Plus Dynamics®, respectively. While some submodels, including the thermodynamic framework, can be inserted directly into the Aspen Plus® GUI, others must be implemented as FORTRAN user models. Physical property user models are developed for viscosity, density, surface tension, and diffusivity. The kinetics, interfacial area, and mass transfer coefficient models are also implemented as user models.

3. NCCC STEADY STATE VALIDATION

A total of 23 steady-state test runs were performed at the NCCC. In addition to encompassing a large range of process operating conditions (e.g., solvent temperature and composition, liquid and gas flowrates, and stripper reboiler duty), the test runs vary the number of absorber beds used (1-3) and the presence or absence of intercooling between the beds. When comparing the model predictions with the experimental data, no model parameters are tuned to improve its fit. Although frequently models are tuned to match pilot scale data, doing so limits the applicability of the model to other scales and operating conditions. The absorber simulation is evaluated for all cases, and the results are compared with experimental values of CO₂ capture percentage in Figure 3.

![Figure 3 – Parity plot for percentage of CO₂ capture in 23 absorber simulations. Maximum and average percent errors are 9.19% and 3.62%, respectively.](image)

Furthermore, the model effectively captures the wide variety of absorber temperature profiles observed in the data. For example, a comparison is shown in Figure 4 for a case in which the model correctly predicts the temperature rise near the top of the column where the CO₂ absorption occurs and the relatively flat temperature profile toward the bottom of the column. In this simulation, the absorber is modeled by 90 stages, and the relative column position represents the normalized stage number, where values of 0 and 1 are the top and bottom of the column, respectively. The bulges in the temperature profile that occur around column positions of 0.33 and 0.67 represent the effect of intercooling.

![Figure 4 – Example absorber temperature profile model and data comparison. Absorber has 3 beds with 2 intercoolers and L/G = 1.41 in mass units](image)

For the stripper model, the lean loading of the solvent in the column outlet is compared with the data for all cases, and a parity plot is shown in Figure 5. A comparison of the experimental and model temperature profiles in the stripper for one case is shown in Figure 6. This column was modeled with 40 stages, and the column position is represented in normalized form by the same technique used in the absorber model.
Figure 5 – Parity plot for lean solvent CO₂ loading in 23 regenerator simulations. Maximum and average relative deviations are 8.09% and 2.69%, respectively.

Figure 6 – Example regenerator temperature profile model and data comparison for case with solvent flowrate of 7300 kg/hr and reboiler duty of 430 kW.

4. RATE-BASED MODEL APPROXIMATION

For dynamic simulation, the model developed in Aspen Plus is exported to Aspen Plus Dynamics. However, Aspen Plus Dynamics does not support the rigorous rate-based model. In order to achieve reasonable accuracy, Murphree efficiencies are approximated using the results from the rate-based model and used to adjust the equilibrium calculations in the dynamic model. In this work the approach developed by Zhang et al. (2015) is further extended and the following correlation is regressed over a wide range of gas and liquid flows and compositions to obtain the Murphree efficiencies:

\[
\varepsilon = A \left( \frac{F_L}{F_L^o} \right)^B \left( \frac{F_V}{F_V^o} \right)^C \left( \frac{CO_2_{load}}{CO_2_{load,o}} \right)^D \left( \frac{MEA}{MEA_o} \right)^E
\]

where \(F\) is the flowrate, \(CO_2_{load}\) is the ratio of moles of CO₂ per mole of MEA in the liquid phase, \(MEA\) is the MEA mass fraction in the liquid phase. The subscript \(o\) indicates a reference state of these variables, and the subscripts \(L\) and \(V\) indicate liquid and vapor phases, respectively. \(A, B, C, D\) and \(E\) are parameters regressed to fit the conditions of the column profile using the method of least squares. The equation is then implemented in the equilibrium model in Aspen Plus Dynamics to approximate the rate-based results. Figure 7 shows the comparison between the rate based model and the equilibrium model enhanced with the Murphree efficiency model for CO₂ flowrate from the top of the absorber.

5. DYNAMIC PILOT PLANT TEST RUNS

There is a lack of dynamic data for pilot plant scale MEA-based CO₂ capture processes in the open literature. The data that are available span a limited range of operating conditions and often only contain a single step change. With this motivation, dynamic data were collected from NCCC following a protocol designed to capture process nonlinearity. The inputs that were varied include the flowrates of the solvent, inlet flue gas, and reboiler steam.

5.1 Dynamic Data Reconciliation Methodology

The dynamic data collected from the NCCC pilot plant were found to have significant measurement noise and some inaccurate measurements. In addition, there were a number of key variables that were unmeasured. To handle these issues, a dynamic data reconciliation (DDR) framework is developed to ensure closure of material and energy balances prior to model validation.

The DDR formulation is represented by:

\[
\begin{align*}
\min(\eta - \tilde{\eta})^T\psi^{-1}(\eta - \tilde{\eta}) \\
\text{s.t.} \quad & \dot{x}(t) = f(x(t), z(t), u(t), t) \\
& g(x(t), y(t), z(t), u(t), t) \leq 0 \\
& \eta(t) = [y(t); u(t)]
\end{align*}
\]

where, \(\eta, x, z, y,\) and \(u\) represent the reconciled, differential, algebraic, measured, and input variables. \(\psi\) is the covariance matrix and overtilde ‘~’ denotes measured variables. Before being used for DDR, noisy data sets are pre-processed using a combination of band-pass and moving average filters.

The optimization problem is implemented in Aspen Plus Dynamics and solved using a feasible path algorithm.

6. RESULTS

Figure 8 shows the reconciled input for the test run when the lean solvent flowrate is perturbed. Even though a constant flue gas flowrate is desired under this test condition, it exhibits some noise as shown in Figure 9.
Figure 10 shows the reconciled data for CO₂ capture percentage as a result of the step changes in lean solvent flowrate shown in Figure 8. The model accurately captures the dynamics of the process with the exception of the transients in the process at the beginning of the step tests before introducing any perturbations. Obviously, the process was not at steady state when the step tests were initiated. Model predictions for a number of additional dynamic test runs (not shown here) are also found to be satisfactory.

Data preprocessing followed by a DDR methodology is found to be efficient for handling a large set of dynamic data with a high noise to signal ratio, as the reconciled results showed a significant improvement compared with the unreconciled results. The high level of accuracy observed in the results demonstrate that the Murphree efficiency-based approach for approximating the results from the rate-based model is satisfactory when applied to dynamic test runs with similar operating conditions. The proposed model can capture most of the process nonlinearities and satisfactorily predict the transient behavior of the process in response to a diverse set of perturbations. The accurate predictions of the model will not only allow for a greater degree of confidence during plant scale up, but also can be leveraged to develop an advanced control framework for the solvent based CO₂ capture process.

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7. CONCLUSION

In this work, submodels for physical properties, thermodynamics, transport, and mass transfer have been developed using the data from lab-scale, wetted wall columns and bench scale systems. The resulting process model is validated with data obtained from the NCCC. Importantly, the model is validated without the need to tune any model parameters, demonstrating the predictive capability of the underlying submodels. During the steady-state test runs, the number of beds in the absorbers was varied to change the scale of the system and the model is found to accurately predict system behavior. Thus, discrepancy in the model due to scale up is found to be minimal for this system.

Data preprocessing followed by a DDR methodology is found to be efficient for handling a large set of dynamic data with a high noise to signal ratio, as the reconciled results showed a significant improvement compared with the unreconciled results. The high level of accuracy observed in the results demonstrate that the Murphree efficiency-based approach for approximating the results from the rate-based model is satisfactory when applied to dynamic test runs with similar operating conditions. The proposed model can capture most of the process nonlinearities and satisfactorily predict the transient behavior of the process in response to a diverse set of perturbations. The accurate predictions of the model will not only allow for a greater degree of confidence during plant scale up, but also can be leveraged to develop an advanced control framework for the solvent based CO₂ capture process.

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