

Rate-Based Modeling and Economic Optimization of Next-Generation Amine-based Carbon Capture Plants

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Abstract

Amine scrubbing processes remain an important technology for mitigating the contribution of carbon emissions to global warming and climate change. Like other chemical processes, they can benefit from computer-aided optimization at the design stage, but systematic optimization procedures are rarely employed due to the challenges of simulating the requisite rate-based models. This paper presents a novel approach for the simulation and optimization of rate-based columns, with specific application to the absorber and stripper columns found in (amine-) solvent-based carbon capture processes. The approach is based on pseudo-transient continuation, and the resulting column models are easily incorporated into large-scale process flowsheets with other previously developed pseudo-transient models. We demonstrate that the proposed approach allows for gradient-based optimization of next-generation amine scrubbing processes by optimizing a complex carbon capture process for three different operating conditions. The results provide general insight into the design of amine scrubbing processes, and shadow prices at the optimal point suggest potential avenues to improve the process economics. The effects of carbon dioxide removal percentage and flue gas composition on process economics are briefly analyzed.

Keywords: Carbon capture, pseudo-transient simulation, flowsheet optimization, rate-based modeling, amine scrubbing, cost optimization

1 Introduction

Carbon emissions are a major contributor to global warming and climate change, and human-generated carbon emissions continue to increase with energy demand across the globe. As a result, carbon capture and sequestration, or CCS, remains a key technology for mitigating the effects of anthropogenic carbon emissions. Post-combustion CCS processes can greatly reduce the CO₂ emissions of existing coal and natural gas power plants. The Petra Nova facility, an absorption-based plant that captures 90% of the CO₂ from a flue gas stream, retained a million tons of CO₂ in just over six months of operation¹. CO₂ captured by the Petra Nova project is utilized in enhanced oil recovery (EOR), one of many applications for captured CO₂. Such applications provide additional economic motivation for carbon capture, sequestration, and utilization (CCSU) with amine scrubbing. While the current scale of captured CO₂ utilization is small (and dominated by EOR), continued research and development driven by increased supply is expanding utilization

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areas²: urea manufacturing, beverage carbonation, and refrigeration have all been identified as significant opportunities. Additionally, new productive uses of carbon dioxide, such as microalgae cultivation and mineral carbonization, continue to emerge³. The broad applicability of CCS and CCSU, as well as increasing economic opportunities and incentives for utilization, suggest a long-term role for carbon-capture technologies in the future of sustainable energy.

Presently, the technology of choice for post-combustion CO₂ capture is amine scrubbing, which offers flexibility through straightforward scale-up, on/off operation dependent on demand, and retrofit possibilities for existing plants^{4;5}. Although technologically mature, amine scrubbing processes tend to have high capital and operating costs. This has spurred significant research efforts to improve process efficiency through advanced technologies, tight process integration, and process intensification^{6;7;8;9;10}. Research efforts have also targeted decreasing the cost of solvent-based carbon capture by exploring the choice of absorbent¹¹. Historically, monoethanolamine (MEA) has been considered the standard solvent for amine scrubbing processes for post-combustion capture, but piperazine (PZ) has been recently identified as a second-generation solvent because it is resistant to oxidative degradation, less volatile than MEA, and not corrosive to stainless steel^{12;13}. These advantages allow for better energy performance and minimize the impacts of degradation products in piperazine-based processes. The main challenge for PZ-based processes is the potential for precipitate and/or nitrosamine formation⁵. Relatively few studies have been carried out on PZ-based processes¹⁴, and a significant challenge in adapting a PZ-based process is identifying the optimal (e.g., in terms of economic efficiency) process configuration and operating conditions, which are likely different from those of a conventional MEA-based process^{15;16}.

Experimental campaigns are important for identifying promising solvents and associated process configurations for CO₂ capture, but they are expensive and typically limited to small, pilot-scale systems^{15;9}. Consequently, mathematical modeling, simulation, and optimization can play a major role in identifying promising conceptual configurations and designs for carbon capture plants¹⁷. A significant hurdle in applying such computer-aided design tools in the case of amine scrubbing processes is that many commercially available models and software packages employ equilibrium-based predictions of the rate of CO₂ removal from flue gas (in the absorber) and rich absorbent (in the stripper). While equilibrium-based models are in general preferred by the chemical industry, as they can generally be reliably solved, the performance of amine scrubbing processes is dominated by mass transfer kinetics, and rate-based (rather than equilibrium-based) models are needed to make accurate predictions^{18;8}. The solution of rate-based models presents many numerical difficulties, leading most computer-aided simulation and optimization studies on amine based CCS/CCSU to employ less accurate, equilibrium-based predictions. In some cases, reduced-order surrogate models are fitted to reproduce rate-based predictions and/or complicated thermodynamic models, again sacrificing a degree of accuracy for ease of computation¹⁹. Advanced designs of amine scrubbing processes benefit from tight heat integration and multiple material and/or energy streams^{7;8}, further complicating simulation and optimization with standard process flowsheet simulation software^{17;20}.

Motivated by the above, in this work, we introduce pseudo-transient continuation as a numerical method for equation-oriented simulation and optimization of amine scrubbing processes with rate-based column models. Using a time-relaxation-based optimization procedure, we show how the model parameters can be regressed, and the full process flowsheet can be optimized. Though the modeling developments are general, we specifically present an application to a plant utilizing a next-generation solvent (piperazine), as well as next-generation configurations of the absorber (with intercooling and pump-around) and stripping section (with an advanced flash stripper). The primary contributions of this work are:

- A robust pseudo-transient model for rate-based columns, easily incorporated in an existing

library of pseudo-transient models for large-scale process simulation and optimization

- Full process modeling of a next-generation amine scrubbing process with multiple recycle and bypass streams, including reconciliation with a detailed thermodynamic model.
- Application of the above developments to optimize an advanced amine scrubbing carbon capture plant for two practically-relevant flue gas compositions.

The paper is structured as follows: we first present a brief review of related work in the design of carbon capture processes. We then provide relevant background on the application of pseudo-transient continuation to process flowsheet simulation and optimization. The pseudo-transient model for rate-based columns is then introduced. The model assumptions are based on the medium-order model by Walters et al.¹⁴. While their model assumed that several thermodynamic and material properties are constant throughout the column, we account for the spatially-dependent nature of all thermodynamic and material properties. Additionally, the rate constants for mass transfer in different types of random and structured packing are regressed using simulations of a detailed model. The developments are applied to a next-generation process flowsheet that includes absorber intercooling, pump-around, and advanced-flash stripper. We optimize the process for a piperazine-based solvent and show a 14% annualized savings compared to a typical base-case process. We briefly examine the effects of altering the percentage of carbon dioxide removal and the flue gas composition.

2 Literature Review

The literature contains numerous reports of prior research devoted to computed-aided modeling, simulation, and optimization of industrial-scale amine scrubbing plants for CO₂ capture. While the present work addresses recently proposed advanced process configurations (i.e., absorber pump-around, intercooling, and advanced stripper configuration), most past efforts deviate minimally from the conventional process configuration shown in Figure 1. Further improvements to the conventional amine scrubbing process have been identified through pilot-scale experiments^{7;15;13} and *in silico* studies^{21;19;22}, and most works agree that the economically optimal process design is highly dependent on solvent choice and flue gas composition. It is notable that only a limited number of publications have addressed optimization of the entire process flowsheet for amine scrubbing processes, or the simultaneous design of unit operation, process configuration, and operating conditions as we do in this paper.

Among them, Mores et al.²³ used an equilibrium-based model to simultaneously optimize a conventional amine scrubbing process including absorber size and operating conditions. Hasan et al. evaluated both the plant-scale⁸ and multi-scale²⁴ economic impact of absorption using monoethanolamine (MEA) as a solvent. The process was optimized using rate-based models and a decomposition-based procedure, wherein the process and heat integration are optimized separately. Burger et al.¹¹ incorporated solvent design into the process optimization problem, identifying the optimal solvent via a group-contribution method. The approach employed a reduced-order representation of the process and surrogate objective functions to aid in optimization. In a related reduced-order modeling effort, Nuchitprasittichai and Cremaschi²⁵ incorporated process simulation predictions with response surface modeling to simultaneously optimize process design parameters, operating conditions, and solvent concentrations. An artificial neural network was used as a surrogate for the economic objective function. More recently, Mores et al.⁹ optimized a CO₂ capture process simultaneously with a coupled natural gas combined cycle plant. Their study addresses the important issue of integrating carbon capture with a power plant, but the simple configuration of the carbon capture process may limit potential heat integration opportunities. All aforementioned

studies demonstrate potential advantages of computer-based optimization of carbon-capture processes. However, as highlighted above, these previous works rely on many model simplifications and are limited to the conventional process structure shown in Figure 1.

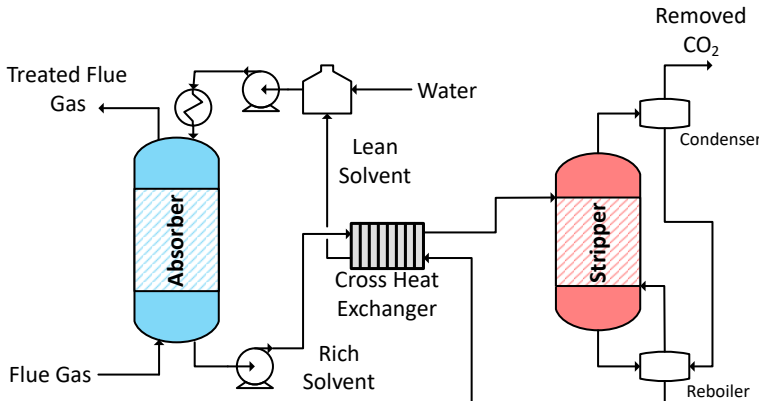


Figure 1: Conventional amine scrubbing process flowsheet

The conventional process (Figure 1) consists of a single absorber column, stripper column, and heat exchanger. The flue gas, from which CO_2 is to be removed, enters the bottom of the absorber column and contacts the down-flowing liquid solvent throughout the column. CO_2 is absorbed into the liquid solution through a reversible, exothermic reaction, and the treated flue gas is released to the atmosphere. The “rich” (having a high absorbed CO_2 concentration) solvent exits the bottom of the absorber and is sent to a stripping column. The stripping column operates at a higher temperature, reversing the absorption reaction. The CO_2 released from the stripper is compressed for sequestration or utilization, while the “lean” (having a low absorbed CO_2 concentration) solvent is recycled to the top of the absorber column. A cross heat exchanger recovers some heat from the lean solvent, reducing the cost of heating the stripper column.

Stripping CO_2 from rich solvent is a particularly energy-intensive operation, and many efforts have been specifically devoted to improving energy efficiency through novel stripper configurations. Alhajaj et al.²⁶ created a comprehensive economic evaluation method and employed equilibrium-based models to optimize and analyze the conventional amine scrubbing process. Optimization was performed by identifying the effect of individual operating parameters on various performance indicators, while holding the remaining operating parameters constant. This univariate sensitivity approach does not account for the interactions/combined effects of these parameters and may not produce the best solution. Damartzis et al.¹⁹ proposed a superstructure-based approach for identifying optimal flowsheet configurations and optimized the process for various solvents using polynomial approximations of thermodynamic equilibrium. Karimi et al.²¹ showed that carefully designed inter-heating in the stripping section can considerably decrease its overall energy requirement. Frailie et al.⁷ examined the energy performance of several alternative stripper configurations, finding that energy efficiency is extremely sensitive to process operating conditions. With a similar motivation, Chen et al.¹⁵ tested replacing the conventional stripper column with a two-stage flash process in an extensive pilot-plant study. Later, Lin and Rochelle¹⁶ performed simulation studies of a combined flash tank and stripper using a rigorous thermodynamic model and found considerable energy savings compared to simple (single-column) stripper configurations. In a more general effort, Oh et al.²² used a superstructure to identify process improvements by introducing additional streams (e.g., absorber intercooling, stream splitting) with a systematic computed-aided optimization procedure. The superstructure was formulated with equilibrium-based models and

solved with a genetic algorithm optimization procedure.

As noted, many of the above works rely exclusively on equilibrium-based predictions. However, Zheng et al.¹⁸ demonstrated the improved accuracy of rate-based models by comparing model predictions with extensive data from an MEA-based, pilot-scale carbon capture process. Several studies have employed such rate-based models: Zhang and Guo²⁷ validated a rate-based model and improved energy efficiency by examining the effects of a few key process parameters. Moioli and Pellegrini²⁸ proposed a rate-based model for piperazine based on Eddy Diffusivity Theory and demonstrated its accuracy through simulations and comparisons with experimental measurements. Also focusing on piperazine, Zhang et al.¹³ created a rate-based model with detailed thermodynamics and a novel stripper configuration, using pilot plant data to validate the model. Notably, in addition to the above uses in steady-state process simulation, rate-based models have also been used for dynamic simulation of carbon capture processes, where they are a necessity to accurately represent the time-dependent behavior of carbon-capture plants. For instance, Mac Dowell and Shah²⁹ conducted dynamic simulations of a coal-fired power plant and an integrated MEA amine-scrubbing unit under various operating regimes. Enaasen Flø et al.³⁰ developed a dynamic model of a similar MEA carbon capture process and validated its performance against pilot plant data, and Walters et al.³¹ developed a reduced-order dynamic model for a piperazine-based process amenable for screening process control strategies.

3 Process Modeling and Design Optimization Background

3.1 General Problem Formulation

The algebraic model of a steady-state chemical process consists of material balances, energy balances, and constitutive equations describing physical properties, phase equilibrium, and/or reaction kinetics. The resulting model can be expressed as a (typically large-scale) nonlinear system of algebraic equations of the form:

$$\mathbf{f}_{ss}(\mathbf{x}, \mathbf{z}, \theta) = 0 \quad (1)$$

where $\mathbf{f} : \mathbb{R}^n \times \mathbb{R}^m \rightarrow \mathbb{R}^n$. $\mathbf{x} \in \mathbb{R}^n$ are the process variables, $\mathbf{z} \in \mathbb{R}^m$ are the design decision variables (e.g., equipment sizes, input flow rate), and θ are the model parameters.

For process flowsheet optimization, it is highly desirable to solve all the nonlinear equations (1) simultaneously (i.e., equation-oriented process simulation), including recycle streams. This approach allows the use of Newton-type algebraic solvers, which exhibit rapid convergence properties. The primary advantage of the equation-oriented approach is that accurate gradient matrices are easily obtained with automatic or symbolic differentiation packages, enabling modern gradient-based optimization procedures. Nevertheless, a well-documented downside to process simulation with Newton-type solvers is that the algorithms require well-informed initial guesses to converge to a solution, and are thus not always robust. The interested reader is referred to Tsay et al.¹⁷ and Mitsos et al.²⁰ for a discussion of process optimization algorithms, challenges, and practices.

3.2 Pseudo-Transient Process Modeling

In addressing the above convergence difficulties, our previous works^{32;33} have established pseudo-transient continuation as a promising numerical technique for steady-state process modeling, simulation, and optimization. In this framework, the steady-state mathematical model of a chemical process flowsheet (1) is converted from an algebraic system of equations to a differential algebraic equation (DAE) system using knowledge about the underlying physical system and is subsequently solved via time integration. The reformulated models exhibit improved convergence properties^{32;34} compared to simulation with standard Newton-type solvers, and several case studies^{35;36;37} have demonstrated their application to complex process optimization. Additionally, the equations of the reformulated DAE system are solved simultaneously, allowing gradient matrices relevant to

optimization to be obtained through automatic or symbolic differentiation. A library of pseudo-transient models for common unit operations, including many of those found in amine scrubbing processes (compressors, flash tanks, heat exchangers, etc.), has been previously developed³². In this section, we briefly describe the application of pseudo-transient continuation to process flowsheet simulation and optimization. The interested reader is referred to our previous works for more detailed discussions of pseudo-transient reformulation^{33;38}, solution procedures^{32;39}, and stability considerations^{32;34}.

A general process flowsheet model, $\mathbf{f}_{ss}$ in (1), is reformulated as an index-one DAE system by converting a subset of the variables $\mathbf{x}_d \subset \mathbf{x}$ to differential variables in a fictitious time domain t . The remaining variables $\mathbf{x}_s = \mathbf{x} \setminus \mathbf{x}_d$ remain algebraic, and the reformulated system can be written as:

$$\mathbf{f}(\dot{\mathbf{x}}_d, \mathbf{x}_d, \mathbf{x}_s, \mathbf{z}, \theta, \tau) = 0 \quad (2)$$

$$\mathbf{g}(\mathbf{x}_d, \mathbf{x}_s, \mathbf{z}, \theta) = 0 \quad (3)$$

where $\mathbf{f} : \mathbb{R}^{n_d} \times \mathbb{R}^{n_d} \times \mathbb{R}^{n_s} \times \mathbb{R}^m \rightarrow \mathbb{R}^{n_d}$ and $\mathbf{g} : \mathbb{R}^{n_d} \times \mathbb{R}^{n_s} \times \mathbb{R}^m \rightarrow \mathbb{R}^{n_s}$ are the set of differential, and algebraic equations, respectively. The choice of $\mathbf{x}_d$ and $\mathbf{x}_s$ is such that $\mathbf{g}(\mathbf{x}_d^0, \mathbf{x}_s, \mathbf{z}, \theta)$ is a full-rank, linear system of equations, and the consistent initialization of the DAE system (2)–(3) can be carried out by a linear solver³². The solution of the original algebraic model $\mathbf{f}_{ss}$ is recovered once the reformulated system $[\mathbf{f}, \mathbf{g}]$ is integrated to steady state. This *static equivalence* property³³ is typically achieved by (i) defining pseudo-transient equations based on first-principles dynamic equations or (ii) introducing first-order filters for equality constraints. Dynamic stability during the integration in pseudo-time is dependent on a careful selection of the time constants τ that define the magnitudes of the dynamics present in the pseudo-transient model^{32;34}. In our recent work³⁹, we also demonstrated that the selection of time constants is based on creating a hierarchy of decoupled (sets of) dynamic equations; we proposed a pseudo-time integration algorithm that replaces defining magnitudes of the time constants with specifying a dynamic hierarchy of the first-order differential equations $\mathbf{f}$ in (2).

In addition to use in process simulation, pseudo-transient models can be used for process optimization. Working in the context of sequential dynamic optimization, Pattison and Baldea³² proposed a time relaxation-based algorithm, in which pseudo-transient integration is used to initialize the process flowsheet model at each optimization iteration. The algorithm proceeds as follows: the model equations are solved by integrating the system, without path constraints, from a set of initial conditions (which reflect an initial guess) for $\mathbf{x}_d$ and $\mathbf{z}$ until steady state is reached. At steady state, the objective function and inequality constraints are evaluated, and their gradients with respect to the decision variables $\mathbf{z}$ are obtained through symbolic or automatic differentiation. The information is passed to a gradient-based optimization solver, which updates the decision variables, and the process is repeated for the new values of $\mathbf{z}$. This procedure proceeds iteratively as described until one or more pre-determined optimization criteria are met. Notably, the equality constraints are solved at each iteration via pseudo-transient time integration, representing a “feasible path” approach³⁴. Optimization is performed only in the reduced space of the decision variables, and global optimization in the reduced space may be possible by automatically propagating McCormick relaxations and subgradients and passing their values to a global optimization solver (in addition to the objective function, inequality constraints, and gradients)⁴⁰.

3.3 Model Reformulation Concepts

Pseudo-transient models can be used to simulate and optimize process flowsheets incorporating detailed models of key units, an approach termed “multiresolution modeling”^{33;41}. The detailed process unit models typically account for distributions in one or more temporal and/or spatial

domain(s), which are discretized using finite difference or collocation schemes. The resulting discretized models have a greatly increased number of variables, and we have introduced pseudo-transient modeling concepts and numerical techniques for robust simulation of these large-scale, discretized systems in previous works^{33;38;34;41}. In this subsection, we review several concepts of pseudo-transient modeling that are relevant to the spatially-dependent, rate-based modeling of packed columns.

Definition of temperature as a state variable. Many expressions in material and energy balance equations are strongly nonlinear functions of temperature. Thus, temperature-dependent variables are a typical source of nonlinearity and a potential cause for inconsistent convergence of algebraic solvers. This issue is addressed by defining temperature as a state (differential) variable. Steady-state energy-balance equations are then converted to ordinary differential equations, where the rate of change of each temperature state variable is proportional to the residual of the static energy balance equation:

$$\tau_i \frac{H_{in}}{T_0} \frac{\partial T}{\partial t} = H_{in} - H_{out} + H_{gen} + Q_{ext} \quad (4)$$

$$T(t = 0) = T_0 \quad (5)$$

where T is the temperature, T_0 is the initial condition (initial guess) for the temperature, and $\tau_i \in \tau$ is an arbitrary time constant. The value of τ_i is set according to stability and convergence considerations^{32;34}. T_0 is typically set to be the inlet temperature to the associated process unit. It is easily verified that the steady state energy balance $0 = H_{in} - H_{out} + H_{gen} + Q_{ext}$ is satisfied by the steady state solution of (4) by setting the time derivative of the temperature T equal to zero.

Dynamic modulation of source and sink terms. Stiffness and nonlinearity in process flowsheet models can also be traced to source and sink terms present in the material and energy balance equations, such as chemical reactions, mass transport, heat transfer, etc. A continuation parameter $\hat{\alpha}$ is introduced in pseudo-transient models to modulate source/sink terms. $\hat{\alpha}$ gradually increases from an initial condition of $\hat{\alpha}(t = 0) = 0$, i.e., the presence of sources/sinks is ignored, to a steady-state value of $\hat{\alpha} = 1$

$$\tau_\alpha \frac{\partial \hat{\alpha}}{\partial t} = 1 - \hat{\alpha} \quad (6)$$

$$\hat{\alpha}(t = 0) = 0 \quad (7)$$

where τ_α is an arbitrary time constant defining the rate at which the modulated terms are introduced, or “turned on”, in pseudo-time. At pseudo-time $t = 0$, source/sink terms multiplied by $\hat{\alpha}$ are modulated to equal zero, simplifying the consistent initialization step. Once the pseudo-transient system is integrated to steady state, the original flowsheet model (1) is recovered and solved, with sources/sinks fully accounted for.

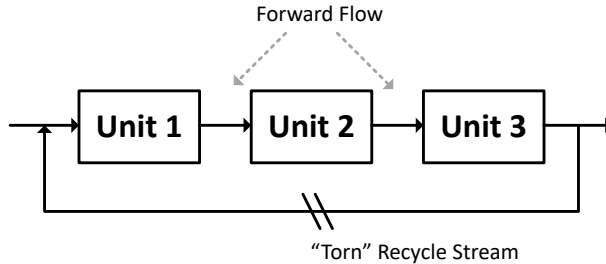


Figure 2: Conceptual depiction of a recycle stream

Pseudo-transient formulation for recycle streams. In addition to challenges arising from solving nonlinear functions, difficult equality constraints may also arise from recycle streams, which introduce algebraic loops. Figure 2 depicts a simple recycle stream example: the outlet conditions of Unit 3 are required to compute the inlet conditions of Unit 1, and vice versa. The system cannot be solved by rearranging or substitution. Similarly, the solvent in the conventional amine scrubbing process flowsheet (Figure 1) is recycled between the absorber and stripper, and must be “torn” to break the algebraic loop. A dynamic “tearing” approach is thus applied to decouple the flowsheet equations representing material and energy recycles.

In particular, initial conditions (guesses) $\mathbf{X}_{tear}^0$ are provided for the upstream state of a recycle stream, and a first-order filter is applied such that the upstream states $\mathbf{X}_{tear}$ and relevant downstream states $\mathbf{X}$ are equal at steady state:

$$\tau_R \frac{\partial \mathbf{X}_{tear}}{\partial t} = \mathbf{X} - \mathbf{X}_{tear} \quad (8)$$

$$\mathbf{X}_{tear}(t = 0) = \mathbf{X}_{tear}^0 \quad (9)$$

τ_R is the recycle time constant, which should be the largest value of any of the pseudo-transient model time constants³³. Providing the initial conditions in (9) allows for explicit calculation of the variables pertaining to the downstream units at the consistent initialization step. During the pseudo-time integration procedure, the tear stream states are (gradually) updated based on the downstream calculated values. At the steady state of the pseudo-transient model, the original flowsheet model (1) is solved, with the upstream and downstream states being equivalent.

4 Carbon Capture Process Modeling

In this work, we consider a piperazine-based carbon capture process flowsheet as described by Freeman et al.⁴². The full process flow diagram, shown in Figure 3 follows the general configuration of the conventional amine scrubbing process (Figure 1), but is significantly more complicated. The process employs an advanced flash stripper—an interconnected flash tank and stripper column—with cold and warm bypass streams. The flue gas stream enters the bottom of the intercooled absorber (C1) at 40°C and 1 atm. *Rich* absorbent exits the bottom of the intercooled absorber (S1) and passes through two heat exchangers, HX1 and HX2, with a cold bypass fraction (S3) removed before HX1 and a warm bypass fraction (S5) before HX2. The remaining stream (S6) is then heated and flashed in F1, with the liquid (S8) *lean* absorbent passed back through HX1 and HX2. The vapor outlet of the flash (S7) passes through a stripper column (C2), after which the vapor (S12) is sent through a third heat exchanger, HX3, and is flashed at 40°C to separate CO₂ and water. The CO₂ (S14) is pressurized to 150 bar for sequestration or utilization, while the water (S15) is sent to a storage tank (T1) to be mixed with the lean absorbent. The cold bypass stream (S3) passes through HX3, is combined with the warm bypass stream (S5), and enters the top of the stripper column (S15).

At intermediate points in the *intercooled* absorber, liquid is drawn out, cooled, and pumped back into the absorber. The location where liquid is pumped back can be above (pumparound) or the same (in-and-out) as the point where it is drawn from the column. As CO₂ is absorbed into the solvent in the absorber sections, the exothermic reaction causes the temperature of the down-coming solvent to increase, and water in the solvent vaporizes. The colder solvent toward the top of the absorber re-condenses water from the vapor phase, and the two phenomena result in a spike in temperature within the absorber, referred to as a “temperature bulge”. Intercooling an absorber reduces the magnitude of the temperature bulge by removing heat at intermediate points. The lower temperature improves the mass transfer rates throughout the column, especially when

the bulge would otherwise occur towards the midpoint of the absorber height⁴³. In-and-out cooling reduces the temperature bulge without increasing the liquid flow rate in sections of the absorber, while pumparound results in increased solvent flow.

The stripping section of the process consists of three heat exchangers, a steam heater, a flash tank, and a stripper column. The split fractions $\eta_1 = \frac{S_3}{S_1}$ and $\eta_2 = \frac{S_5}{S_2}$ (Figure 3) control the fraction of the cold and warm bypasses, which reflect the distribution of the rich absorbent between the flash and the top of the stripper column. η_1 , η_2 , and the size/duty of the heat exchangers are decision variables, and, consequently, the cold and hot bypasses can be removed at decision variable bounds. The heat exchangers can also be removed at these extreme cases, and the optimal point may not contain all three exchangers HX1, HX2, and HX3. The stripper column contains a sump tank at the bottom, where a liquid inventory is maintained for control purposes. We note that while the advanced flash stripper is mathematically modeled as a flash tank and stripper column, in practice, *flashing*, or vapor-liquid separation, can occur in the stripper sump rather than in a separate process unit. Therefore, the flash tank is assumed to not contribute to the capital cost of the full process; rather, its cost is reflected in the cost of the stripper column.

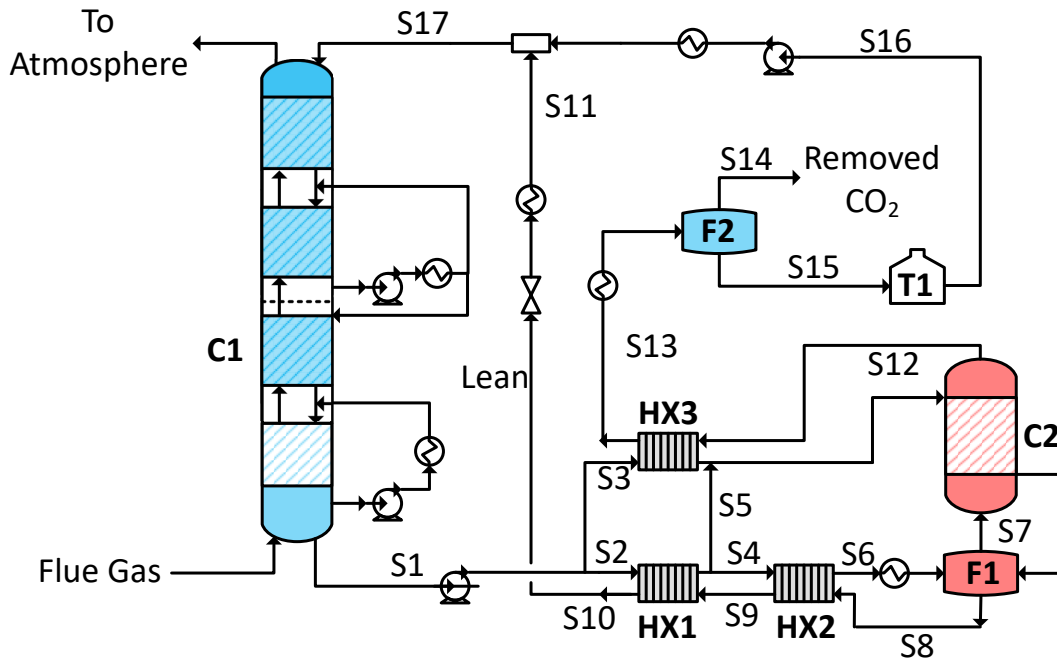


Figure 3: Amine scrubbing process flowsheet.

4.1 Rate-Based Column Model

For the purpose of modeling the carbon-capture plant, we develop a novel pseudo-transient, rate-based model for a packed column, which is used to represent the sections of the absorber and the stripper in the process flowsheet (Figure 3). The model is based on the medium-order model proposed by Walters et al.³¹, which considers variables distributed in the axial domain and represents the bulk liquid and vapor flows in the column using a plug-flow assumption. In this work, we further expand on this model to account for spatially dependent physical properties. The model considers the apparent species (H_2O , CO_2 , and PZ) present in the liquid phase³¹, rather than capturing all true ionic species in the liquid phase. Mass and energy transport are calculated using two-film resistance theory with an apparent species mass transfer coefficient to describe the (unmodeled) boundary layer, as represented in Figure 4. Piperazine is assumed to be nonvolatile,

and oxygen and nitrogen in the flue gas are assumed to be insoluble. Bulk convection is assumed to be negligible, since the flue gas mostly contains oxygen and nitrogen, which are assumed to be insoluble.

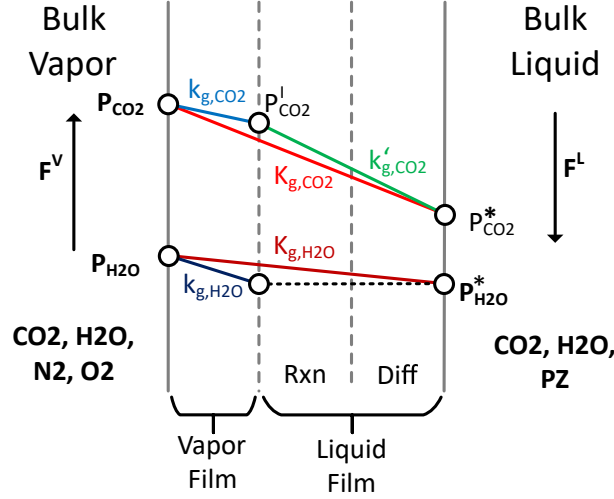


Figure 4: Two-film model for mass/energy transport. Mass transfer occurs at the boundary between bulk vapor and bulk liquid. In the gas film, there is a physical resistance to mass transfer $k_{g,i}$. In the liquid film, a rate-limited chemical reaction (Rxn) and diffusion (Diff) limit the mass transfer of CO_2 . The two liquid resistances are lumped together as k'_{g,CO_2} . The total two-film resistance is denoted as $K_{g,i}$.

4.1.1 Material balances and interphase flux

In each packed section of the absorber and stripper, the axial domain is normalized, such that $z = 0$ at the bottom of the section and $z = 1$ at the top as shown in Figure 5. The model is non-dimensionalized by multiplying the spatial derivatives by the section height L . Assuming no radial variations, the plug-flow mass balance for each absorber section can be written as:

$$\frac{1}{LS} \frac{\partial(x_i F^L)}{\partial z} = N_i^L, \quad i = \text{CO}_2, \text{H}_2\text{O}, \text{PZ} \quad (10)$$

$$\frac{1}{LS} \frac{\partial(y_i F^V)}{\partial z} = N_i^V, \quad i = \text{CO}_2, \text{H}_2\text{O}, \text{N}_2, \text{O}_2 \quad (11)$$

$$\sum_i x_i = 1; \sum_i y_i = 1 \quad (12)$$

where F^L and F^V are respectively the liquid and vapor flow rates, x_i and y_i are the mole fractions, N_i^L , N_i^V represent the molar flux between the bulk liquid and bulk vapor, and $z \in [0, 1]$. S is the cross sectional area of the column. Equation (12) can be reformulated as a pseudo-transient model by defining the flow rates F^L and F^V as dynamic variables:

$$\tau_1 \frac{\partial F^L}{\partial t} = F^L \left(\sum_i x_i - 1 \right) \quad (13)$$

$$\tau_1 \frac{\partial F^V}{\partial t} = F^V \left(\sum_i y_i - 1 \right) \quad (14)$$

$$F^V(t=0) = F_{in}^V, F^L(t=0) = F_{in}^L \quad (15)$$

As shown in Figure 4, material transfer of CO_2 and H_2O occurs between the bulk liquid and

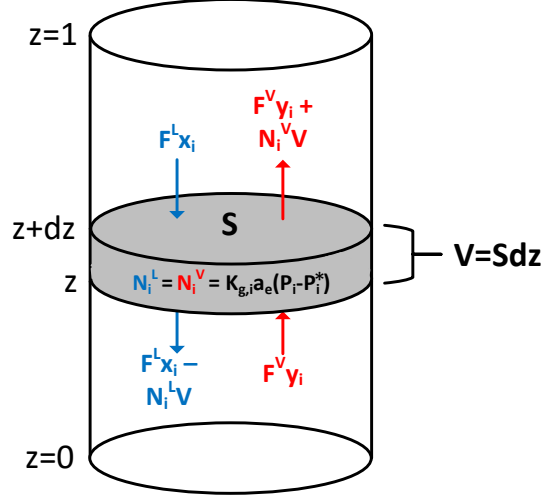


Figure 5: A schematic depiction of plug flow in a packed section. The material flows of component i in and out of a horizontal “slice” of differential thickness dz are shown.

bulk vapor within each section of column packing ($N_{PZ}^L = N_{N_2}^V = N_{O_2}^V = 0$). A linear driving force is assumed for each component flux to define the material transfer rate from bulk vapor to bulk liquid. Additionally, a continuation parameter $\hat{\alpha}$ is introduced to gradually introduce all material and energy fluxes, with dynamics described by (6)–(7).

$$N_i^L = N_i^V = \hat{\alpha} [K_{g,i} a_e (P_i - P_i^*)], i = CO_2, H_2O; 0 < z < 1 \quad (16)$$

where $\hat{\alpha}$ is again a continuation parameter used to modulate the contribution of source/sink terms. P_i is the vapor pressure of component i calculated using Raoult’s law, P_i^* is the equilibrium pressure of component i , and a_e is the effective area of packing. No mass flux is allowed at the ends of the column in order to ensure closure of the total material balance. The height of each column L is accordingly scaled using the height correction suggested by Walters et al.¹⁴ to account for the loss of flux due to this boundary condition. The empirical correlation given by Xu⁴⁴ is used to approximate the equilibrium pressure of CO_2 (17), and the Antoine equation⁴⁵ is used to compute the equilibrium pressure of H_2O (18)

$$P_{CO_2}^* = \exp\left(35.3 - \frac{11054}{T^L} - 18.9\alpha^2 + \frac{4958}{T^L}\alpha + \frac{10163}{T^L}\alpha^2\right) \quad (17)$$

$$P_{H_2O}^* = x_{H_2O} 10^{\left(8.07131 - \frac{1730.63}{T^L - 39.724}\right)} \quad (18)$$

where T^L is the temperature of the bulk liquid and α is the CO_2 loading of the solvent. The *solvent loading* is defined as the ratio between the number of moles of CO_2 absorbed and the number of moles that can be carried by the solvent:

$$\alpha = \frac{x_{CO_2}}{2x_{PZ}} \quad (19)$$

Therefore, the rich absorbent has a high loading (close to 1), while the lean absorbent has a low loading (close to 0).

The mass transfer coefficient $K_{g,i}$ for H_2O is assumed to be equal to the gas film mass transfer coefficient for H_2O , while the mass transfer coefficient $K_{g,i}$ for CO_2 is determined through a series

resistance model:

$$K_{g,H_2O}a_e = k_{g,H_2O}a_e \quad (20)$$

$$\frac{1}{K_{g,CO_2}a_e} = \frac{1}{k_{g,CO_2}a_e} + \frac{1}{k'_{g,CO_2}a_e} \quad (21)$$

where k_{g,H_2O} and k_{g,CO_2} respectively denote the gas film mass transfer coefficients of H_2O and CO_2 . a_e denotes the effective mass-transfer area, which depends on the type of contact surface, or *packing*, used in the column. k'_{g,CO_2} represents the mass transfer coefficient of the liquid phase, a combination of the kinetic resistance from a finite reaction and the physical resistance from the diffusion of reactants and products to and from the vapor/liquid interface. A power law expression fitted to experimental data is used to calculate gas film resistances for structured column packing¹⁴, and a linear relationship is regressed to compute k'_{g,CO_2} as a function of loading. The effective area for liquid-side mass transfer is calculated according to Tsai et al⁴⁶:

$$k_{g,i}a_e = \left(\frac{1.07 \times 10^6}{RT^V} \right) (v^V)^{0.506} \left(\frac{D_{i,flue}}{10^4} \right)^{0.667}, i = CO_2, H_2O \quad (22)$$

$$\ln(k'_{g,CO_2}) = c_1 - c_2\alpha \quad (23)$$

$$\frac{a_e}{a_p} = 1.34 \left(\frac{\rho^L g^{1/3} |F^L|}{\sigma C^L L_p^{4/3}} \right)^{0.116} \quad (24)$$

where T^V is the temperature of the bulk vapor, and v^V is the velocity of the bulk vapor. $D_{i,flue}$ is the diffusion coefficient of component i in the flue gas, calculated using a mole-weighted average of binary diffusion coefficients computed using the Chapman-Enskog equation⁴⁷. a_p is the nominal geometric area of the contact surface (packing), ρ^L is the liquid density, F^L is the liquid flow rate, σ is the surface tension, C^L is the liquid molar concentration, and L_p is the wetted perimeter of the packing. The rate constants c_1 and c_2 are fitted to data from a detailed, species-based thermodynamic model, as described in Section 4.2.

4.1.2 Energy balances and heat transfer

Assuming no radial variations, the energy balance for each absorber section can be written as:

$$\frac{1}{LS} \frac{\partial(H^L F^L)}{\partial z} = N_H^L \quad (25)$$

$$\frac{1}{LS} \frac{\partial(H^V F^V)}{\partial z} = N_H^V \quad (26)$$

where H^L is the molar enthalpy of the liquid flow, H^V is the molar enthalpy of the vapor flow, and N_H^L and N_H^V represent the heat flux between the bulk liquid and bulk vapor. Physical properties packages can typically evaluate enthalpy as a function of temperature, pressure, and composition. In order to instead compute temperature as a function of enthalpy, the temperatures of the bulk liquid and vapor phases, respectively denoted at T^L and T^V , are modeled using first-order pseudo-transient equations³⁸:

$$\tau_2 \frac{H_{in}^V}{T_0^V} \frac{\partial T^V}{\partial t} = H^V - H^{PP,V}(T^V, P, y) \quad (27)$$

$$\tau_3 \frac{H_{in}^L}{T_0^L} \frac{\partial T^L}{\partial t} = H^L - H^{PP,L}(T^L, P, x) \quad (28)$$

where $H^{PP,L}$ and $H^{PP,V}$ denote the liquid and vapor enthalpies computed by a physical properties package using the appropriate equation(s) of state. The heat flux from the vapor phase to the liquid phase is calculated assuming only a gas film resistance due to the relatively high thermal conductivity of liquids. The gas/liquid interface temperature is assumed the same as that of the bulk liquid, and the rate of energy transfer can be written:

$$N_H^L = \hat{\alpha} \left[\sum_i N_i^L (\hat{H}_i^V + \Delta H_{i,abs}) + ha_e (T^V - T^L) \right] \quad (29)$$

$$N_H^V = \hat{\alpha} \left[\sum_i N_i^L (\hat{H}_i^V) + ha_e (T^V - T^L) \right] \quad (30)$$

where $\hat{\alpha}$ is the same continuation parameter for source/sink terms. The vapor enthalpy of each component is computed based on its heat capacity, and the heats of absorption for CO₂ and H₂O are calculated from equilibrium pressures (17)–(18) for thermodynamic consistency:

$$\hat{H}_i^V = Cp^V (T^V - T_{ref}) \quad (31)$$

$$\Delta H_{CO_2,abs} = -R(-11054 + 4958\alpha + 10163\alpha^2) \quad (32)$$

$$\Delta H_{H_2O,abs} = R1730.63 \frac{\log(10)}{(1 - 39.724T^L)^2} \quad (33)$$

The convective heat transfer coefficient ha_e is computed using the Chilton-Colburn analogy as a function of the gas film mass transfer coefficient for H₂O:

$$ha_e = k_{g,H_2O} a_e \left(\frac{RT^V}{100} \right) (C^V Cp^V)^{1/3} \left(\frac{10^4 \kappa^V}{D_{H_2O,flue}} \right)^{2/3} \quad (34)$$

where Cp^V and κ^V are respectively the heat capacity and thermal conductivity of the vapor phase.

4.2 Model Parameter Estimation

In this subsection, we discuss the approach that was used to regress the parameters of the model described in Section 4.1. Unless otherwise noted, the physical properties of the flue gas and the vapor phase of the stripper column were computed assuming ideal gas behavior. The physical properties of the absorbent were computed with the SAFT equation of state. The gSAFT⁴⁸ implementation was used with default parameters, as has been used in other recent works on carbon capture process simulation^{11;19;49}. The general model reconciliation workflow involves simulating a model with detailed thermodynamics and kinetics, collecting relevant data, and regressing the parameters of the model described here to fit the collected data.

An AspenPlus⁵⁰ model was previously developed by Frailie⁵¹ with rigorous thermodynamics and kinetics. The rigorous thermodynamic model explicitly considers liquid-phase speciation, and the model has been fitted to experimental amine pK_a , CO₂ solubility, heat capacity, and amine volatility data for the PZ-H₂O-CO₂ system by regression of Gibbs free energy, enthalpy, heat capacity, and activity coefficient parameters within the electrolyte non-random two liquid (e-NRTL) framework. Due to the aforementioned difficulties of commercial process simulators, the model uses separate simulations for the rate-based models of the absorber (modeled with 90 stages) and stripper (modeled with 35 stages). The two simulations are used in combination to produce cost-optimized configurations of the full carbon capture process.

4.2.1 Intercooled Absorber

The intercooled absorber considered consists of four packed sections, each modeled as described in Section 4.1. The full absorber configuration is shown in Figure 6. The bottom section (Packing

section 4 in Figure 6) consists of Mellapak 2X (MP2X) structured packing, while the remaining sections consist of Mellapak 250X (MP250X) structured packing. Other packing types can be modeled by substituting the appropriate geometric specifications⁵².

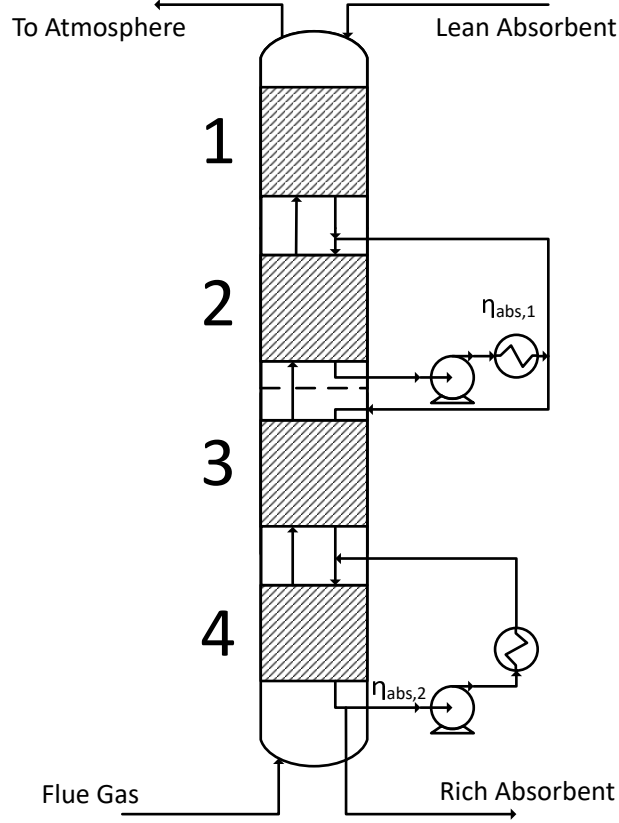


Figure 6: Flowsheet for absorber with four packed sections and intercooling

Two different absorber configurations based on the work of Freeman et al.⁴² were simulated with the AspenPlus model: one designed for 90% CO₂ removal and the other for 99% removal. Both absorbers were assumed to have a 15m diameter⁴². The parameters to describe k'_{g,CO_2} for the pseudo-transient model in (23) were regressed using data from the two different absorber simulations by minimizing the squared deviation from the rigorous model predictions:

$$\min_{c_1, c_2} Error \quad (35)$$

$$Error = \int_z \frac{T^L - T_{Ind}^L}{T_{Ind}^L} + \int_z \frac{T^V - T_{Ind}^V}{T_{Ind}^V} + \sum_i \int_z \frac{F_i - F_{i,Ind}}{F_{i,Ind}} \quad (36)$$

The value for c_2 in (23) was enforced to be the same throughout the column, as it is related to the solvent kinetics and should not change with the packing type. The value for c_1 is related to the liquid diffusive resistance of the packing⁴⁶ and was allowed to differ between the MP250X and MP2X sections. The optimal values found were $c_1 = -4.96$, $c_2 = 13.34$ for the MP250X packing and $c_1 = -5.60$, $c_2 = 13.34$ for the MP2X packing. The agreement between the temperature and vapor concentration profiles of the pseudo-transient model and the rigorous AspenPlus model is generally very good, and a comparison between the fitted model and the training data is shown in Figure 7. Furthermore, the same simulations were repeated with a smaller diameter of 13.5m

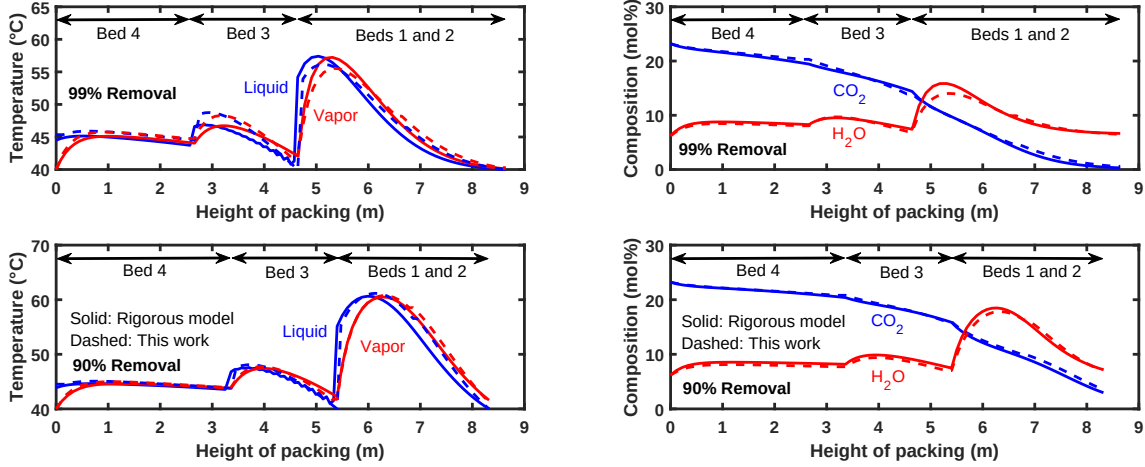


Figure 7: Absorber temperature profiles and gas concentrations for simulations used to train k'_{g,CO_2} parameters. The solid lines correspond to the values predicted by the rigorous AspenPlus model, which were used to fit the model. The dashed lines correspond to predictions from the fitted model.

(packed section heights were adjusted to achieve 90% and 99% removal) to test the prediction accuracy of the regressed model, and the results are shown in Figure 8. The temperature and vapor concentration profiles predicted by the two models are very close, even on the generated test data, suggesting that the developed model can make accurate predictions for a range of absorber diameters and heights.

4.2.2 Stripper Column

The stripper is used to remove absorbed CO_2 from the solvent and return lean absorbent to the absorber. The stripper column consists of a single packed section, filled with Raschig SuperRing No. 0.5 (RSR#0.5) random packing⁵³. The stripper mathematical model has the same structure as that of the absorber, but differs in some important details. First, the effective area of the random packing is calculated differently from that of structured packing, and (24) is replaced with an appropriate correlation for random packing⁵⁴:

$$\frac{a_e}{a_p} = 1.41 \left(\frac{\rho^L g^{1/3} v^{L4/3}}{\sigma a_p^{4/3}} \right)^{0.116} \quad (37)$$

Second, the expression for k_g given in (22) is scaled by a factor cs_1 for random packing, and new values of k'_g are regressed for the stripper. The mass transfer parameters are expected to be different in the stripper, as bulk convection may occur (the gases present are soluble) and mass transfer occurs in the reverse direction (i.e., CO_2 flows from vapor to liquid in the absorber and from liquid to vapor in the stripper). Oxygen and nitrogen are absent in the stripper, and the gas film mass transfer coefficients of H_2O and CO_2 , as calculated by (22), are equal:

$$k_{g,ia_e} = cs_1 \left(\frac{1.07 \times 10^6}{RT^V} \right) (v^V)^{0.506} \left(\frac{D_{i,flue}}{10^4} \right)^{0.667}, i = CO_2, H_2O \quad (38)$$

$$\ln(k'_{g,CO_2}) = cs'_1 - cs'_2 \alpha \quad (39)$$

Two different stripper configurations were simulated with the rigorous AspenPlus model based on the 90% CO_2 removal and 99% removal absorber designs. Both were simulated assuming a

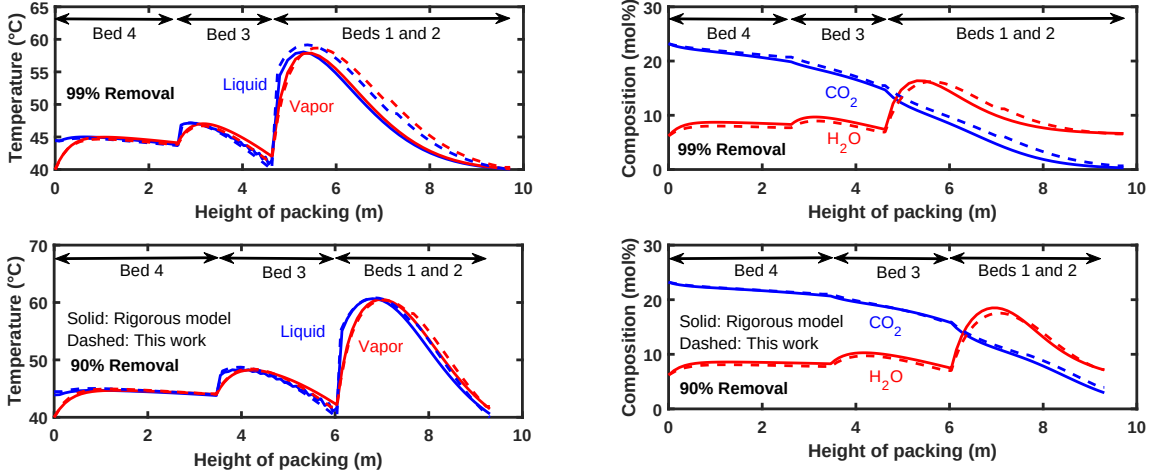


Figure 8: Absorber temperature profiles and gas concentrations for simulations used to test the fitted k'_{g,CO_2} parameters. The solid lines correspond to the values predicted by the rigorous AspenPlus model, using different heights and diameters from the training data in Figure 7. The dashed lines correspond to predictions from the fitted model.

15m column diameter⁴². The parameters to describe k'_{g,CO_2} in (23) were regressed using data from the two stripper simulations by minimizing the squared deviation from the high-order model predictions.

The optimal values found were $cs_1 = 0.25$, $cs'_1 = -0.03$, and $cs'_2 = 34.19$ for the RSR#0.5 packing. The agreement between the temperature and vapor concentration profiles between the regressed model and rigorous Aspen Plus simulations is not as good as in the case of the absorber model. The inaccuracy can possibly be attributed to the contribution of bulk convection to mass transfer, since the vapor in the stripper is composed of soluble components. Further, the correlations employed are developed based on absorber data, since fewer previous works in experimental and modeling have been devoted to the modeling of stripper behavior. Nevertheless, the stripper comprises a much smaller portion of the capital cost than the absorber, and inaccuracies in the model are less likely to impact the optimal process design. A comparison between the fitted model and the training data is shown in Figure 9.

4.3 Other Process Unit Models

In addition to the absorber and stripper, the process flowsheet (Figure 3) contains two flash tanks (F1, F2) and three heat exchangers (HX1, HX2, HX3). Pseudo-transient models for flash tanks and heat exchangers have been previously developed by Pattison and Baldea³² as part of a library of common unit operations, and the models are used in this work with a few minor modifications described here. The vapor fractions in the flash tank F1 were calculated with the methodology described by Madan et al.⁵⁵ for PZ-CO₂-H₂O systems at high pressure and temperature:

$$\ln(P_{CO_2}) = 35.5 - 11054 \frac{1}{T} - 18.9\alpha^2 + 4958 \frac{\alpha}{T} + 10163 \frac{\alpha^2}{T} \quad (40)$$

$$\ln(P_{H_2O}) = 73.6 - 7258 \frac{1}{T} - 7.3\ln(T) + 4.2 \times 10^{-6} T^2 \quad (41)$$

The second flash tank F2 separates only CO₂ and H₂O, and vapor-split fractions were computed with gSAFT. The model for heat exchangers HX1, HX2, and HX3 is given by equations (42)–(47). The temperatures of the outlet streams are calculated using first-order differential equations, as

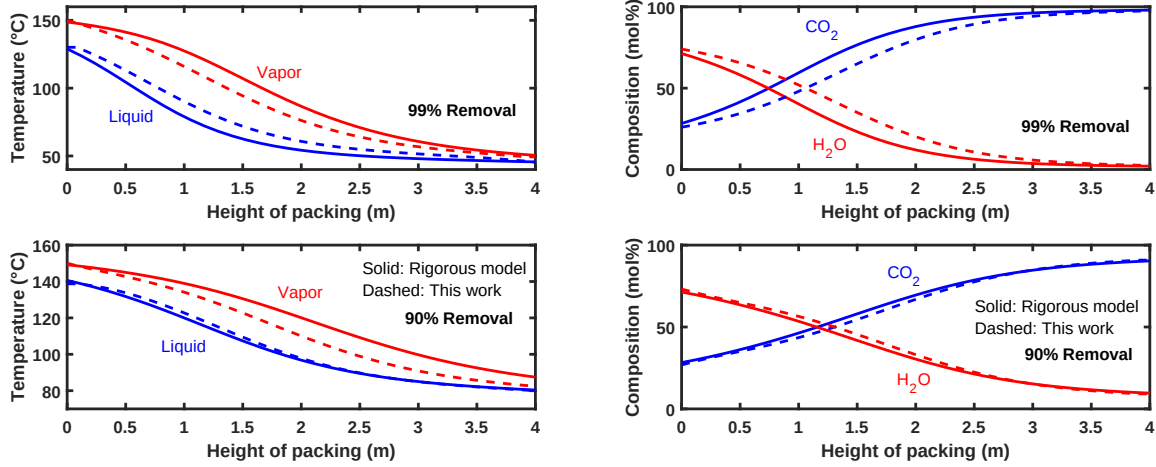


Figure 9: Stripper temperature profiles and gas concentrations for simulations used to train $k_{g,i}$ and k'_{g,CO_2} parameters. The solid lines correspond to the values predicted by the rigorous AspenPlus model, while the dashed lines correspond to the fitted model.

proposed by Pattison and Baldea³². The Underwood approximation⁵⁶ (44) was used to define the driving force for heat transfer, as it has better numerical properties than the log mean temperature difference⁵⁷.

$$H_{out}^h = H_{in}^h - Q \quad (42)$$

$$H_{out}^c = H_{in}^c + Q \quad (43)$$

$$Q = UA \left(\frac{(T_{out}^h - T_{in}^c)^{1/3} + (T_{in}^h - T_{out}^c)^{1/3}}{2} \right)^3 \quad (44)$$

$$\tau_3 \frac{H_{in}^h}{T_0^h} \frac{\partial T_{out}^h}{\partial t} = H_{out}^h - H^{PP}(T_{out}^h, P_{out}^h, z^h) \quad (45)$$

$$\tau_3 \frac{H_{in}^c}{T_0^c} \frac{\partial T_{out}^c}{\partial t} = H_{out}^c - H^{PP}(T_{out}^c, P_{out}^c, z^c) \quad (46)$$

$$T_{out}^h(t=0) = T_0^h, T_{out}^c(t=0) = T_0^c \quad (47)$$

where the superscripts h and c refer to the hot and cold streams respectively. Note that (44) is used since log mean temperature difference $(\Delta T_A - \Delta T_B)/\ln(\Delta T_A/\Delta T_B)$ is indeterminate if $\Delta T_A = \Delta T_B$ at any point during the pseudo-transient time integration. The overall heat transfer coefficients U of all three heat exchangers were assumed to be constant at $800 \text{ W/m}^2/\text{K}$, a value that is similar to that found in other works^{9;58}. The same value of U was used for all three heat exchangers to avoid optimal design solutions that consist of diverting flow (via cold and warm bypasses) to exchangers with higher overall heat transfer coefficients.

5 Carbon Capture Process Optimization

5.1 Design Optimization Problem Formulation

The cost of the carbon capture plant has two components: capital cost (CAPEX) and operating cost (OPEX). The main contributors to CAPEX are the absorber, stripper, heat exchanger(s), steam heater, and compressor. The cost of the flash tank F1 was not included, since the flash is typically not a separate process unit as explained earlier. The Tsai method⁴⁶ was used to calculate

the purchased equipment cost (PEC) of the absorber and stripper. The method is based on raw materials costs, and the estimate was scaled by a factor of 5.0 to represent PEC. The PEC of heat exchangers was calculated by assuming a fixed price of \$22.16 per square foot. Linear scaling (as opposed to a power law) is reasonable, as heat exchanger area is typically increased by adding heat exchangers in parallel for a plant of the capacity considered here. Economic correlations based on a survey of vendor prices^{7;16} were used to estimate the PEC of the steam heater and the compressor.

The OPEX consists of heating, cooling, and electricity costs. Heating costs were calculated by assuming a steam cost of 0.2 cents per MJ, cooling costs were assumed to be 0.063 cents per MJ, and the cost of electricity was assumed to be \$100 per MWh. We note that while the heating costs were assumed to be constant, in reality they may be related to the opportunity cost of electricity production for the integrated power plant. The total annualized capital cost can be calculated from PEC using expression (48)¹⁶. The scaling factor a converts PEC to total capital (installed) cost, while the factor b annualizes the cost. Direct cost, indirect cost, and working capital are included in a , and return on investment, taxes, depreciation, and maintenance are included in b . The values recommended by Lin and Rochelle¹⁶ of $a = 5$ and $b = 0.2$ were used.

$$\text{Total annualized capital cost} \left(\frac{\$}{\text{yr}} \right) = a \times b \times PEC(\$) \quad (48)$$

The decision variables for the design of the intercooled absorber (Figure 6) are the diameter of the absorber, the heights of packed sections 1–4, and the split fractions $\eta_{abs,1}$ and $\eta_{abs,2}$. For the design of the stripping section, the decision variables are the diameter of the stripper, the height of the stripper, and the temperature and pressure of the flash tank F1. Finally, the process-level decision variables include the flowrate of solvent, the sizes of the heat exchangers (HX1, HX2, and HX3), the cold bypass fraction $\eta_1 = S3/S2$, and the warm bypass fraction $\eta_2 = S5/S4$. A complete list of decision variables with associated lower and upper bounds is provided in Table 1. We emphasize that all decision variables, including unit-level and flowsheet-level decisions, were optimized simultaneously.

The solvent was assumed to have a fixed amine concentration of 5 molal piperazine. Although a higher concentration of piperazine may increase the solvent capacity, pilot plant studies¹³ showed that 5 molal piperazine outperforms higher concentration solvents due to lower solvent viscosity (enhanced diffusion and turbulence). In carrying out the design optimization calculations, the following constraints were enforced:

- The CO₂ removal was constrained to be at least 90%, i.e., $Removal = \frac{F_{CO_2,in}^V - F_{CO_2,out}^V}{F_{CO_2,in}^V} \geq 0.9$.
- The heat exchangers were constrained to have a minimum temperature difference (minimum approach) of at least 1°C, i.e., $\Delta T_{min} = \min(T_{h,out} - T_{c,in}, T_{h,in} - T_{c,out}) \geq 1^\circ C$.
- The flooding ratios of both the absorber and stripper were constrained to be 70% or lower, i.e., $\frac{\max(F^V)}{F_{flood}^V} \leq 0.7$, where F_{flood}^V is the flooding point vapor flowrate.
- The pumparound ratios were constrained to be 50% or lower, since pressure losses in the absorber were excluded, i.e., $\eta_{abs,1}, \eta_{abs,2} \leq 50\%$.
- The temperature of the flash tank was constrained to not exceed 150°C in order to avoid thermal degradation of the solvent, i.e., $T_{F1} \leq 150^\circ C$.
- The total bypass ratio of the plant was constrained to not exceed 50% to be consistent with pilot plant results⁵⁹, i.e., $\frac{S3+S5}{S2} \leq 0.5$.

Column flooding refers to excessive vapor flow that causes liquid to be entrained and carried upward. Close to the flooding point (defined as $F^V \approx F_{flood}^V$), the vapor velocity is high enough to carry an excessive amount of liquid upwards. This form of backmixing causes the column performance to decrease, and it also results in a sharp increase in column pressure drop. The flooding ratio $\frac{\max(F^V)}{F_{flood}^V}$ can be decreased by increasing the column diameter, which increases F_{flood}^V by dispersing vapor flow over a larger cross-sectional area (at the cost of a larger, more expensive column).

In carrying out design optimization calculations, we first consider the case where a membrane system is used in conjunction with the amine scrubbing process (for a discussion and overview of membrane and hybrid-membrane systems, the reader is directed to recent papers by Freeman et al.⁴², Bui et al.⁵, and Tian et al.¹⁰). The hybrid configuration allows the amine scrubbing process to benefit from a higher inlet CO₂ concentration and potentially operate at a higher lean-loading state. We begin with this case since a carbon capture plant design heuristically optimized for 90% removal is available as a reference point⁴². The reference base case process, shown in Figure 10 has a 12.9 kmol/s inlet flue gas flow rate, with the stream containing 23.2mol% CO₂, 6.2mol% H₂O, 69mol% Nitrogen, and 1.6mol% Oxygen. We employed the pseudo-transient models in Section 4.1 to model the process flowsheet, using finite differences in the reverse direction of flow to approximate the spatial partial derivatives in the absorber and stripper. Each section of the absorber was discretized using 20 finite difference points (80 total points), while the stripper was discretized using 50 finite difference points.

The resulting model has 10068 equations and was implemented in gPROMS version 5.1.4⁶⁰, using the built-in DASOLV package for time integration. The selection of pseudo-transient time constant values is generally based on dynamically decoupling the model equations³². Therefore, the values of the time constants are selected to create a hierarchy of decoupled pseudo-transient dynamics of different orders of magnitude: $\tau_1 = 1$ in (13)–(14), $\tau_2 = 10$ in (27), and $\tau_3 = 1000$ in (28), (45)–(46). The value of the time constant for the continuation parameter is set to $\tau_\alpha = 0.1$ in (6), and the dynamic tearing time constant is set to $\tau_r = 10000$ in (8). Simulation of the base case is completed in 272s of CPU time using a 64-bit Windows 10 desktop system with a 3.20GHz Intel Core i7 processor and 16GB of RAM. The values of the decision variables in the base case are presented in Table 1, and the economic costs are presented in Table 2. The base case design removes 90% of CO₂ from the flue gas stream, representing a capture of 4.12 million tons of CO₂ per year (\$28.40 per ton of CO₂). The absorber operates at 67% flooding, while the stripper operates at 30% flooding. The minimum temperature approaches of HX1, HX2, and HX3 are respectively 15.00°C, 15.00°C, and 36.51°C.

5.2 Optimization Results

5.2.1 Case 1: Base Case Optimization

The process was optimized using a time-relaxation-based approach optimization³² with the sequential quadratic programming algorithm (NLPSQP) in gPROMS⁶⁰. The base case was used as the initial guess, and the optimal solution was found in 5551s of CPU time (58 NLP iterations). While the CPU time required for this study is large, we note that recent results suggest that the pseudo-transient state integration time (> 99.9% of CPU time) can be reduced by orders of magnitude by decoupling the dynamic equations of the system³⁹ or attempting solution of the original steady-state algebraic model during optimization iterations⁶¹.

The optimal values of the decision variables and economics of the optimal design are shown in Table 1 and Table 2. The optimal flowsheet is also shown in Figure 10. At the optimal point, 90% of CO₂ from the flue gas stream is removed, representing a capture of 4.12 million tons of CO₂ per year (\$24.47 per ton of CO₂). The annual cost of the process and the cost per ton of CO₂ are both reduced by 14% compared to the base case. The absorber and stripper both operate at 70% flooding

	Lower Bound	Base Case	Optimal Point	Upper Bound
Intercooled Absorber				
Absorber Diameter (m)	0	15.00	13.59	-
Section 1 Height (m)	0	1.46	2.15	-
Section 2 Height (m)	0	1.46	1.59	-
Section 3 Height (m)	0	2.30	3.56	-
Section 4 Height (m)	0	3.36	0.00	-
Split 1 $\eta_{abs,1}$ (%)	0	0.0	32.0	50
Split 2 $\eta_{abs,2}$ (%)	0	50.0	0.0	50
Stripping Section				
Stripper Diameter (m)	0	13.05	8.74	-
Stripper Height (m)	0	4.00	4.92	-
Flash Temperature ($^{\circ}\text{C}$)	0	150	150	150
Flash Pressure (bar)	1.01325	5.80	5.80	12
Cold Bypass η_1 (%)	0	6.0	4.0	50
Warm Bypass η_2 (%)	0	35.0	40.0	50
Other Process Decisions				
Solvent (S17) Flow (kmol/s)	0	89.12	93.53	-
HX1 Area (m^2)	0	23472	14157	-
HX2 Area (m^2)	0	27453	37555	-
HX3 Area (m^2)	0	260	802	-

Table 1: A comparison between base-case and optimal-point values for the process design variables for the case of 90% CO_2 removal from a rich flue gas stream.

	Base Case		Optimal Point	
Capital Cost (PEC)	\$Million	contribution	\$Million	contribution
Absorber	18.11	15.5%	14.23	14.1%
Stripper	7.96	6.8%	5.17	5.1%
Exchangers	12.21	10.4%	12.53	12.4%
<i>HX1</i>	<i>5.60</i>		<i>3.38</i>	
<i>HX2</i>	<i>6.55</i>		<i>8.96</i>	
<i>HX3</i>	<i>0.06</i>		<i>0.19</i>	
Compressor	13.92	11.9%	13.93	13.8%
Steam Heater	2.08	1.8%	1.22	1.2%
Operating Cost	\$Million/yr	contribution	\$Million/yr	contribution
Heating	32.27	27.6%	22.32	22.1%
Cooling	6.37	5.4%	7.28	7.2%
Electricity	24.11	20.6%	24.14	23.9%
Totals	\$Million/yr	contribution	\$Million/yr	contribution
CAPEX	54.28	46.4%	47.07	46.7%
OPEX	62.76	53.6%	53.74	53.3%
TOTAL	117.03	100.0%	100.82	100.0%

Table 2: A comparison of process economics between base-case and optimal-point values for the case of 90% CO_2 removal from a rich flue gas stream.

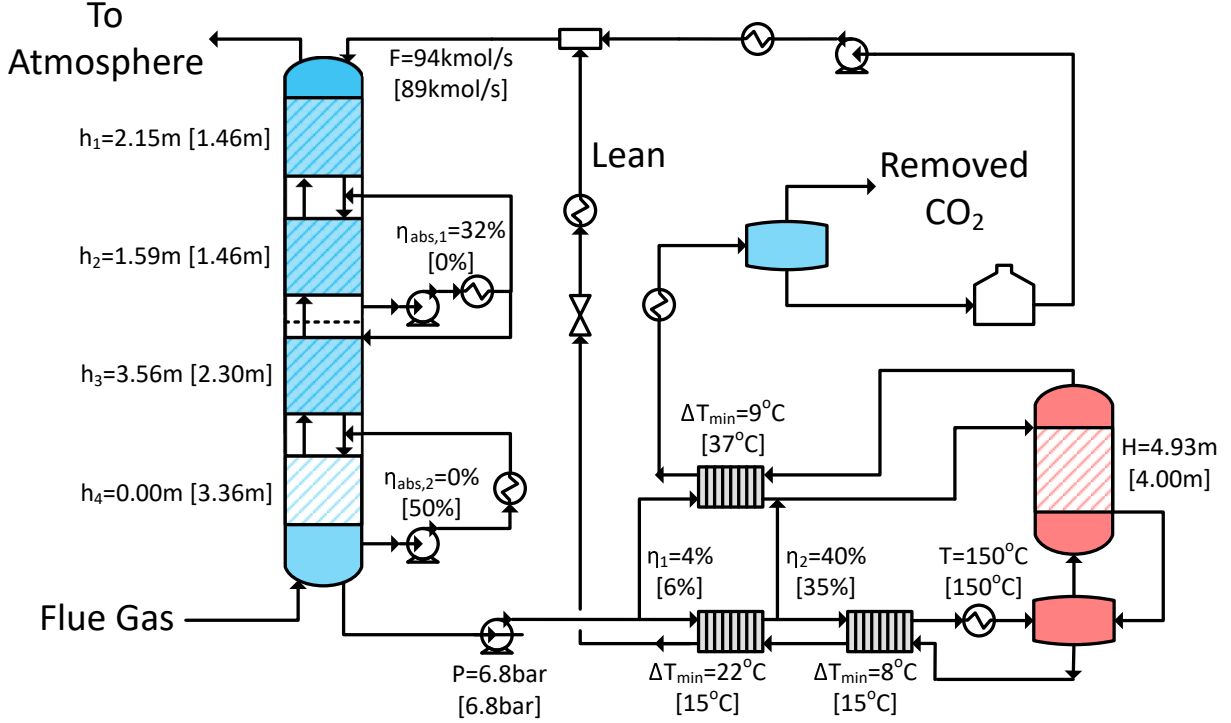


Figure 10: Base case and optimal design of the amine scrubbing process flowsheet. Base case values are shown in square brackets.

ratio, and their diameters are slightly reduced. The minimum approach temperatures of HX1, HX2, and HX3 are respectively 21.79°C, 8.16°C, and 9.25°C. These design changes are non-obvious, with computer-guided optimization procedure increasing the minimum approach temperature of HX1 and decreasing those of HX2 and HX3. Correspondingly, the size (and contribution to capital cost) of HX1 decreases from the base case to the optimal point, while the sizes of HX2 and HX3 increase.

Regarding heat integration, the manipulation of heat exchanger sizes and bypasses slightly decreases the temperature of the warm bypass from 83°C in the base case to 79°C at the optimal point. The rich absorbent exits HX2 (S6) at 142°C, compared to 127°C in the base case, and the heating costs make up a much smaller percentage of overall annual cost. The drop in warm bypass temperature is compensated for by increasing the temperature of the cold bypass stream (S3) exiting HX3 from 64°C in the base case to 82°C at the optimal point. This increase is partially accomplished by decreasing the cold bypass ratio. The majority of the savings come from a reduction in heating costs, which are the main contributor to OPEX in the base case process. The heat use is decreased from 3.72GJ to 2.57GJ per ton of CO₂, a number consistent with the best pilot plant results⁵⁹.

The profiles of key variables along the absorber are shown in Figure 11. Both the absorber and stripper have smaller volume compared to the base case and make up a smaller proportion of the overall annual cost. Compared to the base case design, the height of the absorber is decreased at the optimal point, while removing the same amount of CO₂. The optimized absorber benefits from a decreased temperature bulge in the upper sections: the maximum liquid temperature in the base case absorber is 61.3°C, compared to 53.5°C in the optimal design. The bottom section of 2X packing with pumparound is not present at the optimal point, while 32% of the liquid at the bottom of the packed section 2 (Figure 6) is pumped back to the top of the section, greatly lowering the temperature in the top section of the absorber.

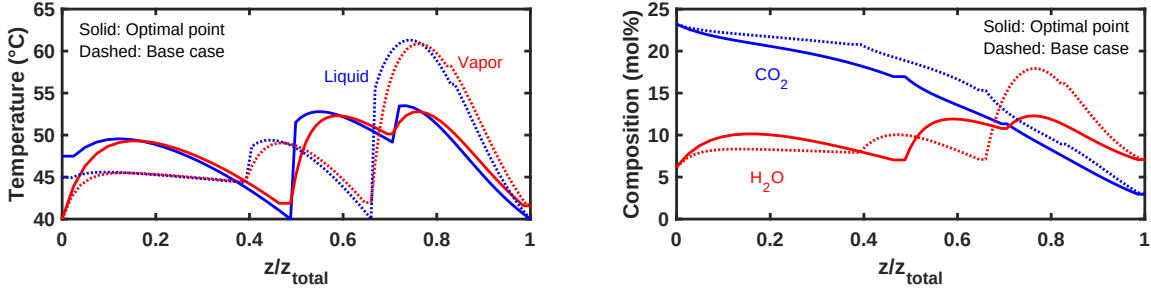


Figure 11: A comparison of absorber temperature and vapor composition profiles between base-case and optimal-point designs. The solid lines correspond to the optimal point design, while the dashed lines correspond to the base case design. The narrow “flat” regions between packed sections reflect the height correction described in Section 4.1.

At the optimal point, only one decision variable reaches its upper or lower bound: the flash temperature reaches its maximum allowed value of 150°C to in turn maximize the vapor flow through the stripper column. The associated Lagrange multiplier at the optimum (shadow price) is $0.64 \text{ \$Million}/^{\circ}\text{C}$. The shadow price p_s is defined as

$$p_s = \frac{\partial OBJ}{\partial x^b} \quad (49)$$

where OBJ is the objective function and x^b is the value of the active constraint. The shadow price reveals that the local estimated effect of increasing the upper bound of temperature in the flash tank by 1°C is a decrease in total cost of $\$0.64$ million per year ($\$0.155$ per ton of CO_2 removed), providing insight into the benefits of improving the thermal stability of the solvent. This value can also guide the economic feasibility of operating the process at a higher temperature and constantly replacing part of the piperazine solvent that undergoes thermal degradation. The percentage of CO_2 removed from the flue gas stream also reaches its lower bound, and the shadow price of CO_2 removal is $1.24 \text{ \$Million}/\%$. Correspondingly, the local estimated effect of increasing the removal by 1% (0.046 million tons of CO_2 per year) is $\$1.24$ million per year, or $\$27.13$ per additional ton of CO_2 removed.

5.2.2 Case 2: Optimization for Increased Removal

To examine the cost of increased removal for the same flue gas stream and hybrid-membrane process, the same optimization procedure was repeated with the CO_2 removal constrained to be at least 99%. Starting from the same initial guess, the optimal point was found in 50 NLP iterations, using 5287s of CPU time on the same desktop system. The optimal values of the decision variables and economic costs of the optimal design are shown as Case 2 in Table 3 and Table 4. The decision variable values from Case 1 above are also reproduced for comparison. Compared to the optimal point found in Case 1, the heights of Sections 1, 2, and 3 in the absorber are increased to achieve the requisite 99% CO_2 removal. Interestingly, the diameter of the absorber is slightly decreased in the solution, compared to the optimal point found for Case 1. The bottom section of MP2X packing with pumparound is again not present at the optimal point. The optimal design removes 99% of CO_2 from the flue gas stream, representing a capture of 4.53 million tons of CO_2 per year ($\$25.27$ per ton of CO_2). The absorber and stripper both operate at a 70% flooding ratio, and the minimum approach temperatures of HX1, HX2, and HX3 are respectively 22.85°C , 6.76°C , and 9.28°C .

Compared to the solution of Case 1, the minimum approach temperature of HX1 is further

	Case 1	Case 2	Case 3
Intercooled Absorber			
Absorber Diameter (m)	13.59	13.35	12.94
Section 1 Height (m)	2.15	3.60	2.12
Section 2 Height (m)	1.59	2.38	1.52
Section 3 Height (m)	3.56	4.07	2.45
Section 4 Height (m)	0.00	0.00	0.00
Split 1 $\eta_{abs,1}$ (%)	32.0	20.3	47.7
Split 2 $\eta_{abs,2}$ (%)	0.0	0.0	0.0
Stripping Section			
Stripper Diameter (m)	8.74	9.56	7.29
Stripper Height (m)	4.92	4.75	4.49
Flash Temperature ($^{\circ}\text{C}$)	150	150	150
Flash Pressure (bar)	5.80	5.68	5.52
Cold Bypass η_1 (%)	4.0	4.2	4.6
Warm Bypass η_2 (%)	40.0	44.9	47.6
Other Process Decisions			
Solvent (S17) Flow (kmol/s)	93.53	102.15	58.89
HX1 Area (m^2)	14157	14494	8971
HX2 Area (m^2)	37555	41342	21711
HX3 Area (m^2)	802	866	548

Table 3: Optimal-point values for the process design variables for Case 1 (base case optimization), Case 2 (increased removal), and Case 3 (lean flue gas).

increased by 1.1°C , while that of HX2 is further decreased by 1.4°C . The minimum approach temperature of HX3 remains practically unchanged from Case 1 to Case 2. The manipulation of heat exchanger sizes and bypasses again slightly decreases the temperature of the warm bypass from 83°C in the base case to 80°C at the optimal point. The temperature of the rich absorbent exiting HX2 (S6) is increased to 143°C , and the heating costs are again decreased compared to the base case. However, the heating costs are increased compared to the optimal solution of Case 1. The relative heat use at the optimal point increases slightly from 2.57GJ per ton of CO_2 in Case 1 to 2.64GJ in Case 2, indicating a slight tradeoff between process removal and efficiency in terms of heat use.

The design for 99% removal requires a significantly larger absorber, and, consequently, the absorber comprises a larger percentage of the overall annualized cost. The solvent flow rate is also increased, resulting in larger process utility costs. The capital expenditure makes up a similar fraction of the overall cost as in the optimal design for 90% removal. As suggested by the increasing specific heat duty, the increase in CO_2 removal percentage results in a 3.3% increase in the average cost per ton of CO_2 captured. However, considering only the additional CO_2 captured (0.41 tons per year), the cost is \$33.27 per ton, a 36% increase in cost per ton of CO_2 compared to the base amount of CO_2 captured. The shadow price of increasing the upper bound of temperature increases to 0.78 \$Million/ $^{\circ}\text{C}$ (\$0.172 per ton of CO_2 removed), suggesting that improving the thermal stability of the solvent has increasing benefits as CO_2 removal is increased. The percentage of CO_2 removed from the flue gas stream reaches its increased lower bound of 99%, and the shadow price of CO_2 removal is 2.96 \$Million/%. The large increase in shadow price of CO_2 removal reveals that the cost of removing additional CO_2 also increases with CO_2 removal.

	Case 2		Case 3	
Capital Cost (<i>PEC</i>)	\$Million	contribution	\$Million	contribution
Absorber	17.91	15.6%	11.46	17.5%
Stripper	5.81	5.1%	4.05	6.2%
Exchangers	13.53	11.8%	7.45	11.4%
<i>HX1</i>	<i>3.46</i>		<i>2.14</i>	
<i>HX2</i>	<i>9.86</i>		<i>5.18</i>	
<i>HX3</i>	<i>0.21</i>		<i>0.13</i>	
Compressor	15.45	13.5%	8.08	12.4%
Steam Heater	1.45	1.3%	0.68	1.0%
Operating Cost	\$Million/yr	contribution	\$Million/yr	contribution
Heating	25.23	22.0%	14.63	22.4%
Cooling	8.29	7.2%	4.991	7.6%
Electricity	26.79	23.4%	14.00	21.4%
Totals	\$Million/yr	contribution	\$Million/yr	contribution
CAPEX	54.15	47.3%	31.71	48.5%
OPEX	60.31	52.7%	33.63	51.5%
TOTAL	114.46	100.0%	65.34	100.0%

Table 4: Process economics for Case 2 (increased removal) and Case 3 (lean flue gas).

5.2.3 Case 3: Optimization for a Lean Flue Gas Stream

The same process was then optimized in a scenario reflecting CO₂ removal by an amine scrubbing process alone, without membrane pre-treatment of the flue gas. A lean flue gas stream typical of post-combustion processes⁸ was assumed, and the CO₂ removal was constrained to be at least 90%. The inlet flue gas flowrate to the amine scrubbing process assumed to be 12.9 kmol/s, with molar composition of 13.2% CO₂, 9.5% H₂O, 73.3% Nitrogen, and 4% Oxygen. The optimal point was found in 50 NLP iterations, using 5091s of CPU time on the same desktop system, and is shown as Case 3 in Table 3 and Table 4. The optimal design removes 90% of CO₂ from the flue gas stream, capturing 2.58 million tons of CO₂ per year (\$25.33 per ton of CO₂). The absorber and stripper both operate at 70% flooding ratio, and the minimum approach temperatures in HX1, HX2, and HX3 are respectively 23.73°C, 5.95°C, and 10.39°C. The increase in removal results in a 3.5% increase in the cost per ton of CO₂ captured, compared to the hybrid membrane process.

The process design is significantly changed compared to the solution found for a hybrid-membrane process (Case 1). The minimum approach temperature of HX1 is further increased by 1.9°C, and that of HX2 is further decreased by 2.2°C. The minimum approach temperature of HX3 is slightly higher compared to the solution of Case 1, but still much lower than the base case value. In contrast to the solutions for Cases 1 and 2, the temperature of the warm bypass is increased from the base case, up to 84°C at the optimal point. The warm and cold bypass streams have increased temperatures, as the solvent flow rate is significantly decreased. Heating costs are still lowered with the increase in temperature of the rich absorbent exiting HX2 (S6) to 144°C. This high temperature is in part enabled by a large warm bypass of almost 48% at the optimal point. The heating costs comprise a similar proportion of the overall annual cost as in the solutions to Cases 1 and 2. The relative heat use at the optimal point increases dramatically from 2.57GJ per ton of CO₂ in Case 1 to 2.96GJ in Case 2, demonstrating the value of pre-treating the flue gas stream for higher CO₂ concentration in terms of process efficiency.

Though it captures less CO₂, the design for the leaner (in terms of CO₂ concentration) flue

gas requires a relatively large absorber, and the absorber comprises a much larger percentage of the overall annual cost. The bottom section of 2X packing is again not present at the optimal point, but the highest fraction of pumparound is required of all three cases to achieve the requisite CO₂ removal. The solvent flow rate is greatly decreased, and utility and HX costs are decreased. The cost of the compressor and electricity use also decreases, as there is less carbon dioxide to pressurize. The capital expenditure makes up a larger fraction of the overall cost, compared to the other optimal designs presented, since the contributions of the absorber and stripper to overall cost are increased.

The shadow price of increasing the upper bound of temperature decreases to 0.43 \$Million/°C. While the magnitude of the shadow price decreases, the per unit shadow cost (\$0.167 per ton of CO₂ removed) remains similar to those found in the previous cases. Therefore the per unit value of improving the thermal stability of the solvent is relatively constant across all three optimal process designs. The percentage of CO₂ removed from the flue gas stream reaches its lower bound of 90%, and the shadow price of CO₂ removal is 0.83 \$Million/%. Correspondingly, the local estimated effect of increasing the removal by 1% (0.029 million tons of CO₂ per year) is \$0.83 million per year, or \$28.95 per additional ton of CO₂ removed. This shadow price reveals that the cost of removing additional CO₂ is larger for the case of a standalone amine scrubbing process compared to the hybrid-membrane process (Case 1), further demonstrating the value of a higher concentration flue gas stream.

5.2.4 General Observations

All the optimal designs found in this work operate at several bounds: (i) the absorber and stripper always operate at the maximum 70% flooding ratio, which allows their diameters to be minimized; (ii) the temperature of the flash tank is always at its maximum allowed value of 150°C, a limitation imposed by the thermal stability of the amine-based solvent; and (iii) packed section 4 of the absorber, consisting of Mellapak 2X packing is never present. We note that the MP2X packing may introduce less pressure drop than Mellapak 250X, but pressure losses in the absorber were not considered in this work. In the future, the selection of packing can potentially be included as a discrete decision variable during optimization. Furthermore, the costs of the optimal designs found in this work are split relatively equally between CAPEX and OPEX, suggesting that the costs can be significantly decreased by either category. For example, the CAPEX contribution can be decreased if the process lifespan is increased (a longer annualization) or if such carbon capture plants are mass-produced (lowering PEC), and the OPEX can be decreased if electricity subsidies are provided for carbon capture processes.

As shown in Table 3, the optimal designs found in this work are very different from one another. In a similar result, Cerrillo-Briones and Ricardez-Sandoval⁶² found using a robust optimization approach that the optimal design of an absorber column can vary significantly when considering uncertainty in flue gas stream composition and/or desired CO₂ removal. At the optimal points, many decision variables do not reach an upper or lower bound (or they are unbounded), highlighting the necessity of computer-guided optimization procedures in designing the most economic process for a particular operating regime. The hybrid membrane process proposed by Freeman et al. benefits from a higher inlet CO₂ concentration and significantly reduces the per unit cost of carbon capture. We found that the optimal design for the higher-concentration CO₂ flue gas costs 4% less (per ton of CO₂ captured) than the optimal design for a typical post-combustion flue gas stream. Changing the desired CO₂ removal percentage from the flue gas stream has a similar effect on the total cost per ton of CO₂. Increasing the fraction of CO₂ captured only increases the average per unit cost slightly, though the marginal cost of capturing additional CO₂ (added removal) is quite large.

6 Conclusions

In this article, we proposed a new computational framework for rate-based modeling, simulation, and optimization of next-generation carbon-capture processes. We introduced a pseudo-transient numerical approach for modeling rate-based packed columns, with particular application to packed absorbers and strippers. The models are generally applicable to rate-based column modeling and utilize pseudo-transient continuation. As a result of the latter, they are easily combined with other process unit models in a previously developed pseudo-transient process modeling framework in order to optimize process flowsheets incorporating rate-based column models.

The proposed novel models lend themselves naturally to optimization applications, and we exploited this property to regress the models to predictions from a previously developed rigorous thermodynamic and kinetic model. We demonstrated the proposed approach for process optimization by considering a next-generation amine scrubbing process, finding large economic savings in comparison to a previously studied and heuristically optimized base case design. The optimal design varies with the properties of the inlet and outlet flue gas, demonstrate the need for computational tools in finding the optimal plant configuration for each application. Additionally, we confirmed that the percentage of carbon dioxide removed from the flue gas and the concentration of carbon dioxide in the flue gas have large effects on the economic cost (per unit of carbon dioxide) of the optimal design.

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Nomenclature

Greek

α	loading (mol CO ₂ /mol alkalinity)
$\hat{\alpha}$	continuation parameter (dimensionless)
κ	thermal conductivity (MW/m K)
ρ	mass density (kg/m ³)
σ	surface tension (N/m)
τ	pseudo-transient time constant (pseudo-time)

Roman

A	heat exchange area (m ²)
a_e	effective wetted area of packing (m ² /m ³)
a_p	specific area of packing (m ² /m ³)
C	concentration (mol/m ³)
C_p	specific heat capacity (MJ/mol K)
D	diffusion coefficient (cm ² /s)
F	molar flowrate (mol/s)
g	gravitational acceleration (m/s ²)
H	enthalpy (MJ)
h	convective heat transfer coefficient (MW/m ² K)
K_g	overall mass transfer coefficient (mol/bar m ² s)
k_g	gas mass transfer coefficient (mol/bar m ² s)
k'_g	liquid mass transfer coefficient (mol/bar m ² s)
L	height (m)
L_p	wetted perimeter (m)
N	material flux (mol/m ³ s)
N_H	enthalpy flux (MW/m ³)
P	pressure (bar)
P^*	equilibrium pressure (bar)
Q	heat duty (MJ)
R	gas constant (J/mol K)
S	cross-sectional column area (m ²)
t	pseudo-time
T	temperature (K)
U	overall heat transfer coefficient (MW/m ² K)
v	superficial velocity (m/s)
x	liquid mole fraction (mol/mol)
y	vapor mole fraction (mol/mol)
z	height (m/m)

Nomenclature (continued)

Superscripts

c	cold-side
h	hot-side
L	liquid
PP	physical properties package
V	vapor

Subscripts

Ind	Independence model
i	component
in	inlet
out	outlet

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