CHAPTER 3

Industrial Applications of Plant-Wide Equation-Oriented Process Modeling—2010

Milo D. Meixell Jr., Boyd Gochenour and **Chau-Chyun Chen**

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Aspen Technology, Inc., Burlington, MA 01803, USA

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Abstract Mathematical models of industrial processes have long been used to better design and operate facilities. Traditional applications of such models have been limited in scope and usage due to the rapid rise in complexity, execution time, and difficulties encountered as model size increases to encompass sufficient fidelity and scope to address overall economic impact to business units. Simultaneous solution techniques, referred to as equation-oriented (EO) modeling, as opposed to sequential modular (SM) approaches, have addressed many of the issues that previously limited model fidelity and scope across multiple scales from delivering actionable, value-adding results in a frequent, day-to-day, or even hour-to-hour time frame. Models of alkanolamines-based carbon dioxide (CO_2) capture facilities exemplify the ability of EO modeling to include the best high fidelity, multiscale, mechanistic models along with sufficient scope to optimize operations, allowing economic trade-offs among plant throughput and solution regeneration costs, in the context of the larger process that the CO_2 capture system serves. These models span scales from physical and chemical properties of CO_2 and absorbent molecules, process equipment or units, process plants, to site complexes. A steady-state flowsheet model of the CO_2 absorption and solution regeneration system is illustrated and discussed, both in a parameter estimation mode, elucidating system performance from observed plant data, and in an optimization mode, honoring operating constraints, reflecting control system configuration, while maximizing operating profit. The model is also able to help identify and quantify debottlenecking alternatives. The topics of model robustness, accuracy, and execution speed are covered as well. This application illustrates that integrated, high fidelity, multiscale models from molecular level to site-wide complex can be deployed in nonideal online environments to deliver benefits and insight that cannot be elucidated with simpler, less rigorous, more empirical models.

1. INTRODUCTION

Mechanistics-based simulation models of industrial refining and chemical processes have long been used to better design and operate facilities Evans, 2009. However, most traditional applications of such

simulation models have been limited in scope and usage due to the rapid increase in model complexity, execution time, and solution difficulties encountered as model size increases to encompass sufficient scope to address overall economic impact to business units. Linear programming (LP) models are used effectively for large-scope problems. However, LP models include limited fidelity and address planning issues rather than improvement of operating conditions, detailed design, or revamping. Simultaneous solution techniques, referred to as equation-oriented (EO) modeling, as opposed to sequential modular (SM) approaches, have addressed many of the simulation issues that previously limited model scope and fidelity of mechanistics-based simulation models Chen and Stadtherr, 1985; Kisala *et al.*, 1987; Alkaya *et al.*, 2001. Furthermore, significant advances have been made in understanding and modeling detailed mechanistic phenomena that when widely and frequently applied to monitor and improve operations can yield considerable additional revenue from existing assets Cutler and Perry, 1983.

After decades of industrial practice and continued refinement, delivery of model-based, actionable, value-adding operational or design improvement results in an efficient manner offline, or on a frequent, day-to-day, or even hour-to-hour time frame in an online environment is now very achievable and in fact, widely practiced in the industry. Applications range widely including petroleum refineries Liporace *et al.*, 2009; Camolesi *et al.*, 2008; Mudt *et al.*, 1995, petrochemical plants Cutler and Perry, 1983; Rejowski *et al.*, 2009; Paules and Meixell, 1994; Fatora and Ayala, 1992; Fatora *et al.*, 1992a; Fatora *et al.*, 1992; Houk *et al.*, 1992; Kelly *et al.*, 1991 and chemical plants Mercangöz and Doyle, 2008; Lowery *et al.*, 1993; Meixell and Tsang, 1988. This article presents the state of the art in the industrial applications of plant-wide EO process modeling. We discuss the importance of modeling objectives and the significance of specifying model variables. We present steady-state simulation models of different mode: simulation models, optimization models, models for parameter estimation, and models for reconciliation. We highlight various aspects of modeling in industrial practice: model scope, model fidelity, embedded solution strategies, process economics, offline and online usage, and model maintenance. Also discussed are the current industrial applications including critical success factors. While a major driving force for developing simultaneous solution approaches has been to meet the needs for real-time optimization (RTO) applications, including execution speed, robustness, and ease of posing the problem to represent the present process situation, we discuss the much more broad usage

and benefits of these methods. Lastly, we present the details of a particularly relevant process, carbon dioxide (CO_2) capture with alkanolamines, to illustrate that integrated, high fidelity, multiscale models from molecular level to site-wide chemical complex or enterprise level can be deployed in online environments to deliver benefits and insight.

Biegler Biegler, 2009 discussed methods for integrating ''process models over multiple scales, ranging from open-form, declarative models that arise in real-time process optimization to 'black-box' models that characterize molecular simulations.'' While this article does not include molecular simulations or computational fluid dynamics (CFD), it does deal with multiscale models that integrate layers of heterogeneous models across significant differences of physical scale of chemical supply chain National Research Council, 2003 from single and multiphase systems, to process equipment and units, to plants, complexes, and enterprises. Figure 1 shows the types of equations solved in each scale. Such integrated, high fidelity, multiscale process models are essential to gain better process understanding and to achieve optimal design of new plants, revamping of older ones, and operations of existing facilities.

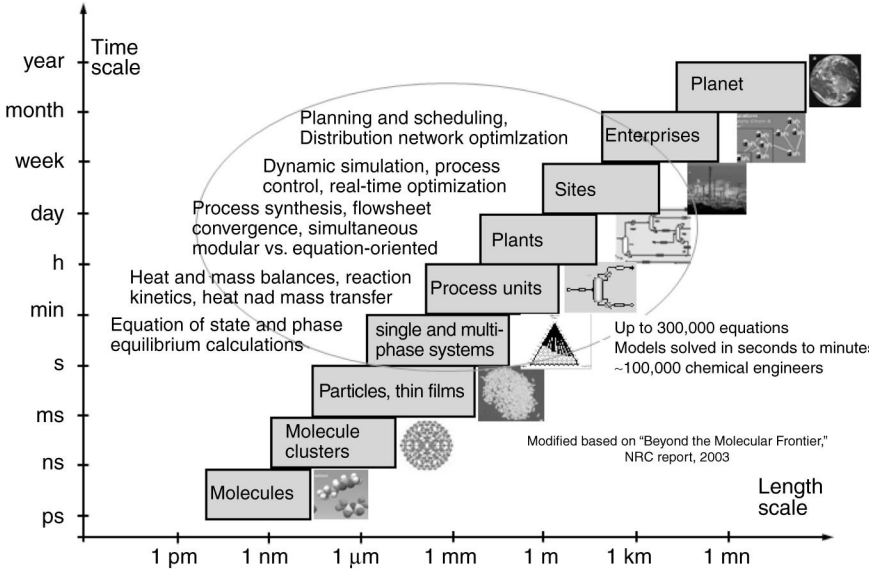

Figure 1 Integrated, high fidelity, multiscale process modeling of chemical supply chain.

2. SEQUENTIAL MODULAR SOLUTION TECHNIQUES VERSUS SIMULTANEOUS SOLUTION TECHNIQUES

Models become more complex as their fidelity and scope increase. As models become more complex, the methods used to solve the model equations become more important. SM solution techniques are adequate for solving models of modest complexity, while models of significant complexity are solved efficiently using simultaneous solution methods Chen and Stadtherr, 1985; Kisala *et al.*, 1987, typically using sparse matrix methods. These simultaneous solution methods pose the equations of the model in ''0 = $f(x)$'' or ''Residual(i) = $f(x)$'' format where the ''0'' is the desired value of the equations' residuals at solution. Models posed in this manner are referred to as ''equation-oriented'' or ''EO'' models. Figure 2 illustrates the relationship between model complexity and modeling difficulty with SM solution method and EO modeling method.

Care should be taken when embarking on a modeling effort to choose the modeling environment and method, which assure that the model is solved efficiently when its complete scope and level of fidelity are reached.

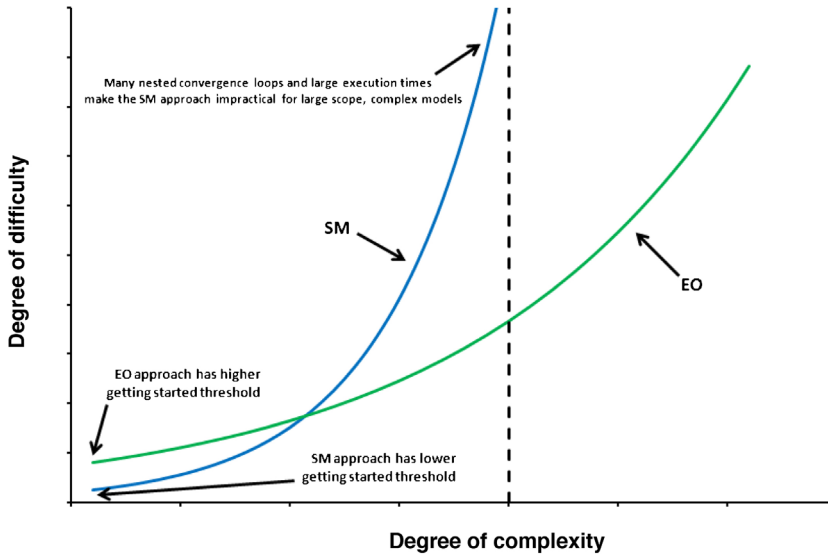

Figure 2 Sequential modular (SM) and equation-oriented (EO) modeling difficulty versus complexity.

3. MODELING OBJECTIVES

It is important to understand the objective or objectives of a modeling undertaking. Some models can be quite useful even if simple, while others require high fidelity and rigorous mechanistic underpinnings to meet their objectives. Some models are not required to be predictive (e.g., models used only for monitoring performance). Others must be predictive to deliver their intended benefits (e.g., models used for optimization). A well-planned modeling undertaking can be designed to meet the immediate requirements while making it easier to extend the model features to meet future requirements.

Some models require dynamic relationships to compute conditions changing in time, while others employ very detailed transport phenomena, such as CFD models. Most, if not all, models have steady-state foundations onto which accumulation terms are added to capture dynamic effects, or onto which transport properties are imposed to investigate detailed flow, composition, temperature, or other property effects in detailed, nonhomogeneous distributions. Since most models require good steady-state models as foundations, the following discussions will focus on steady-state modeling employing rigorous, nonlinear, mechanistic models. Models representing important mechanisms occurring at relatively small scales of composition (which is related to small length scales) capture many causes and effects across wider ranges of operating conditions than models that attempt to bypass the underlying mechanistic steps and pose the model empirically and only deal with larger scales of physical dimension. For example, ionic concentrations in liquids are important at concentration levels far below the concentrations of the species from which they dissociate. Failure to model at these small concentration levels diminishes the accuracy of the macroscopic performance of the equipment models in which these ionic solutions are employed. Similarly, reactions that mechanistically occur homogeneously via free radicals or heterogeneously via adsorbed surface species also are affected profoundly by species concentrations even as low as 10^{-10} mol fraction levels.

4. MODEL VARIABLES

A significant part of developing a model used for other than determining static sets of heat and material balances (which are sufficient for some model objectives, such as providing the basis for new plant design) is specifying which variables are independent and which are dependent. Far more variables are dependent variables than are independent in essentially all models. For simulation and optimization

cases, there is close to a one-to-one correspondence between actual in-the-plant independent variables and model independent variables. Independent variables within a plant are typically boundary conditions (e.g., feed compositions), equipment parameters (such as heat exchanger areas, number of trays in a distillation column, etc.), or conditions that can be set because ''final control elements'' (typically valves) exist to allow controllers to manipulate flows to meet flow set points (flow indicators and controllers, FICs), temperature set points (temperature indicators and controllers, TICs), pressure set points (pressure indicators and controllers, PICs), and analyzer (composition) set points (analyzer indicators and controllers, AICs). There are many measured dependent or ''controlled'' variables in a plant, such as flow indicators (FIs), temperature indicators (TIs), pressure indicators (PIs), and analyzer indicators (AIs).

It is important to have the correct set of variables specified as independent and dependent to meet the modeling objectives. For monitoring objectives observed conditions, including the aforementioned independent variables (FICs, TICs, etc.) and many of the ''normally'' (for simulation and optimization cases) dependent variables (FIs, TIs, etc.) are specified as independent, while numerous equipment performance parameters are specified as dependent. These equipment performance parameters include heat exchanger heat transfer coefficients, heterogeneous catalyst ''activities'' (representing the relative number of active sites), distillation column efficiencies, and similar parameters for compressors, gas and steam turbines, resistance-to-flow parameters (indicated by pressure drops), as well as many others. These equipment performance parameters are independent in simulation and optimization model executions.

Models used in a predictive mode (simulation and optimization) should be validated by comparing their ''steady-state gains'' (many of which are nonlinear across their operating range) to those of the plants they are mimicking, or to reasonable gains experienced in similar equipment configurations. A steady-state gain is the change in a dependent variable for a unit change in an independent variable.

The aforementioned specifications reflect the control system in a plant (existing or under development). The importance of having a model appropriately specified cannot be overstated.

5. SIMULATION

Models used for simulation studies must be predictive. Traditional simulation models are used to design new facilities and to explore alternative conditions and configurations of existing facilities. Models

can be built with basic functionality, such as material balances, and can be improved by adding sufficient detail to meet their intended objectives. Material balances and heat balances can be developed or configured with certainty. Thermodynamic equilibrium relationships, while well known, may just supply limits (constraints) beyond which separation and chemical reactions are not feasible. Rate-based relationships (heat, mass, and momentum transfer) are far more uncertain than thermodynamic state functions and demand more detailed modeling. When simulating an existing facility, a model's predictive performance can be greatly improved by using measurements to update model parameters before simulation. And it is best to validate a model by evaluating its performance parameters at different operating conditions and understanding the sensitivity of simulation results, especially economic ones, to parameter values.

6. PARAMETER ESTIMATION AND RECONCILIATION

Models used for monitoring equipment or process performance do not necessarily need to be predictive, and therefore are considerably less expensive to develop. These kinds of models are typically used solely in parameter estimation or reconciliation modes to track key process indicators (KPIs) or equipment performance. Parameter estimation can be done with a model that is ''square,'' that is, has an equal number of equations and unknowns, whereas reconciliation estimates the same parameters but has degrees of freedom (DOFs) that allow the reconciliation to distribute errors among redundant measurements and uncertain values that are otherwise assumed to be constant, while minimizing a classic least-squares objective function, or a more sophisticated gross error detection (GED) objective function Özyurt1 and Pike, 2004; Tjoa and Biegler, 1991. The DOFs are typically offsets or multipliers between measured and model values and the aforementioned uncertain ''otherwise constant'' variables. These latter DOFs can be variables such as equipment performance ones that have no single measurements that directly reflect their values.

While some reconciliation models only have material balance relationships, more meaningful reconciliation results are obtained with models that include material balances, heat balances, equilibrium constraints (both in the separation and reaction domains), rate relationships (heat transfer, mass transfer, momentum transfer, and kinetics), as well as equipment-specific relationships. In other words, one should include more than just material balance constraints when reconciling a model. Heat balance, kinetics, transport relationships—if needed for the

predictive capability of the model—need to be parameterized in the reconciliation. This is not replacing measurements, but using available measurements for reconciliation to determine optimal model parameters.

7. OPTIMIZATION

A model used for optimization must be predictive, and must have several other features to be an effective tool. Today's optimizers have the model and the solution ''engine'' segregated. Engineers focus on posing the appropriate problems, and are relieved to a great extent of how the optimization problem is solved. Some previous generations of models used for optimization have had the model and optimization algorithms intertwined and were extremely difficult to modify and maintain with changing plant configurations. Today's optimizers almost exclusively use gradient search techniques, and therefore must have continuous functions and first derivatives (the Jacobian) to be efficient and robust. Optimizers that use second derivative information (such as Successive Quadratic Programming (SQP)[4]) require good estimates or direct calculation of the second derivatives (the Hessian) of the equations and the objective function. Optimizers must be able to honor limits of operating conditions so that the solutions are meaningful. These limits are typically imposed as upper and lower limits on both dependent variables and independent DOFs, and if not judiciously imposed can lead to mathematically infeasible problems. The efficiency of solution (number of successive iterations and therefore execution times) is greatly affected by the optimization algorithm and how limits are imposed. Many optimization methods are degraded and even caused to fail by imposing too many unnecessary limits since the path to the solution is affected. Most efficient optimization methods use infeasible path methods, and only require feasibility at the solution. The model equations themselves limit solution values to be between reasonable limits if posed well. For example, there is no need to limit mole fractions to be between zero and one when the model equations are well posed.

DOFs in an optimization case are independent variables that have final control elements, such as valves. These DOFs include FICs, PICs, TICs, and AICs. Objective functions typically are ones that maximize operating profit ($\sum$Product values $-$ $\sum$Feed costs $\pm$ $\sum$Utility costs). The aforementioned objective function can serve well in both sold out and market limited economic environments. The different economic environment can be imposed by simply bringing a product flow limit into play (for the market limited situation) or out of play (for the sold out

situation). In sold out conditions more physical limits (maximum allowable temperatures, pressures, maximum valve openings, product qualities, etc.) become active than in the market-limited environment.

8. SUMMARY OF SIMULATE/OPTIMIZE/PARAMETER/RECONCILE CASES

Most modelers are more familiar with ''Simulate'' cases that generate results with naturally independent variables kept constant and naturally dependent variables being calculated. For models with all relationships (equations) that are universally true, such as material balances and heat balances, Simulate cases are many times sufficient. When equipment-specific performance relationships are integrated into the aforementioned type of models, for new plants Simulate cases may still be sufficient since equipment performance is estimated using best practices, and no actual performance results are available to enhance the estimated performance parameters. For existing facilities, actual plant (including equipment) performance results are available, and can be used as feedback to greatly enhance a model's predictive accuracy. Feedback can be incorporated by solving ''Parameter'' or ''Reconcile'' cases where many variables that were dependent in the aforementioned Simulate cases are now known, and therefore held constant (become independent) while other variables that were independent (equipment performance factors) are now dependent (calculated).

Both the Parameter and Reconcile cases determine (calculate) the same set of parameters. However, these cases do not get the same values for each parameter. A Parameter case has an equal number of unknowns and equations, therefore is considered ''square'' in mathematical jargon. In the Parameter case, there is no objective function that drives or affects the solution. There are typically the same measurements, and typically many redundant measurements in both the Parameter and Reconcile case. In the Parameter case we determine, by engineering analysis beforehand (before commissioning an online system for instance) by looking at numerous data sets, which measurements are most reliable (consistent and accurate). We ''believe'' these, that is, we force the model and measurements to be exactly the same at the solution. Some of these measurements may have final control elements (valves) associated with them and others do not. The former are of FIC, TIC, PIC, AIC type whereas the latter are of FI, TI, PI, AI type. How is any model value forced to be exactly equal to the measured value? The ''offset'' between plant and model value is forced to be zero. For normally independent variables such as plant feed rate, tower

pressures, and so on, that is straightforward, and no ''measurement model'' containing a plant model and offset is really required (but there are many reasons it is a best practice to use a measurement model for all measurements). For otherwise dependent variables (FI, PI, etc.) in a Parameter case, we declare equipment performance parameters to be dependent. This allows these kinds of measurements to be believed and ''square up'' the problem, keeping it well posed. For a measurement that is redundant and cannot be used to update an equipment performance parameter (since another measurement may already be updating that equipment parameter) its offset (plant minus model) is assigned to be dependent, again squaring up the problem. In this process, judgments have been made on where to allocate the model-measurement mismatch (''error'').

A Reconcile case is configured starting from the Parameter case described above. An objective function is added, either a classic least-squares formulation or a more sophisticated GED approach where the contribution to the objective function does not continue to grow for larger and larger model-measurement offsets, but if the offset is large enough, its contribution to the objective function actually decreases. This GED approach is an automated, during-solution equivalent of ''throwing out'' bad data that is so inconsistent that its confidence limits are reduced (standard deviation increased). The specifications of the offsets of the measurements we believe absolutely in the Parameter case are changed from Constant (independent) to Reconcile, which declares them to be DOFs in the Reconcile case. These offsets, as well as the ones associated with the redundant measurements which are already dependent are included in the Reconcile case objective function, along with their 95% confidence limits $(1/\sigma)^2$, where σ is the standard deviation of the measurement. At the solution to this problem offsets that were constant and zero in the Parameter case will be nonzero; consequently error will be distributed differently than in the Parameter case. So the equipment parameters will also be somewhat different. Since the Reconcile case is nonsquare it can honor constraints (upper and lower limits on any set of variables). Unless slack variables are introduced limits cannot be honored in the Parameter case since there are no DOFs; all the equations must be satisfied with a given set of ''knowns.'' Reconcile cases can assure that many undesirable solutions are eliminated. Furthermore, when reconciling there is no need to reconcile the offsets of every variable that had a constant offset in the Parameter case. Judicious choices can be made on which variables to reconcile. Well-designed software includes a convenient set of specification types that allow users to assign appropriate specifications during model development (or ''on the fly,'' driven by data) and then to switch from

Parameter to Reconcile to Simulate to Optimize cases without changing specifications. The great majority of variables are of ''Calculated'' specification. Far fewer are ''Constant,'' and even fewer are DOFs (i.e., of ''Reconcile'' and ''Optimize'' specification). The specifications assigned to variables, their values, their upper and lower limits, along with the Case type (Parameter, Reconcile, Simulate, or Optimize) and an objective function determine the problem that is being posed.

9. MODEL SCOPE

The scope of a model is typically chosen so that it is sufficient to envelop the feeds, product, and utilities to be able to have a meaningful economic objective function. Sometimes it is preferable to include upstream or downstream facilities even in a simple form to be able to use actual feed, product, and utility costs rather than transfer prices.

Smaller scope models, even of individual unit operations, are of course useful in design and monitoring modes. However, larger scope models allow far greater opportunities for meaningful economic analysis and optimization, either of new or of existing plants.

10. MODEL FIDELITY

Typically it is best to develop a model that has just sufficient fidelity to meet the modeling objectives. Care should be taken and informed decisions made to assure that future needs can be met with minimal cost, so at times some preinvestment can be made in a model by including higher fidelity than absolutely required for immediate objectives.

Many modelers may feel that it is necessary to employ quite simplified models for some applications, for instance for models deployed online. Today's high-speed servers and efficient modeling software allow very detailed and high fidelity models to be used online where execution speed and robustness are important. A model that is too simple may cause difficulties when deployed to optimize existing facilities. The optimization benefits are often ''small differences between large numbers'' since the improvement in operating profit will likely be a small fraction of the operating profit itself. Models of sufficient fidelity and accuracy, often across multiple scales, must be deployed to deliver benefits. Models of insufficient fidelity and accuracy may leave a significant fraction of potential benefits uncaptured or worse yet can compute benefits in the simple

model that result in decreased operating profit in the real plant. Typically, the more mechanistic the model the easier it is to understand the causes and effects between operating conditions and operating profit. Troubleshooting is typically more difficult when simplified models are employed. Empirical models have their place even in otherwise high fidelity models. An additional consideration when determining the appropriate modeling approach is maintainability. For example, correlation-based models can be very effective, but may be invalidated by changes to the process.

Sensitivity analysis can be done to understand the impacts of each of the overall model's individual models and equations to the objective function and to the computed optimal operating conditions.

11. EMBEDDED SOLUTION STRATEGIES

Models can have the characteristic of different types and sizes of equation sets relative to a general set of algebraic equations. Some common example situations include physical property models and models containing differential equations. In posing the mathematical problem to be solved, a completely simultaneous solution approach can be used or a ''mixed mode'' that combines specialized solution techniques within the overall EO approach.

There are advantages and disadvantages to using an embedded solution strategy. Two examples of advantages are (1) resolve issues around multiple solutions to the equation set and (2) more efficient solution by exploiting model structure. First, in physical property models employing a cubic equation of state, it is possible to have multiple solutions to the cubic equation. This can present robustness problems if solved simultaneously with all other equations. A dedicated algorithm to solve the cubic equation with logic to select the proper root is a preferred approach. Second, differential equation sets can present highly structured models that can be exploited by dedicated solvers for more efficient solution. The efficiency can result in part by reduction of the number of variables and equations presented to the general EO solution.

Requirements to use embedded solution techniques include giving accurate function and first derivative evaluations for Newton-based methods. Embedded convergence needs to be tight to ensure the results are accurate and precise. However, this can yield longer solution times and make a simultaneous solution approach preferred. Embedded solutions provide a way of reducing the model variables exposed to the overall solution. The modeler should ensure the eliminated

variables are not needed for calculation of constraints, objective function, of model sensitivities.

12. PROCESS ECONOMICS

Accurate representations of the process economics with market and emission constraints are just as important as process modeling. The pricing along with market and emission constraints provide the economic basis and reflect changing business conditions over time. This can allow the optimization of the model to produce novel operating conditions. These economic inputs may be generated with planning and scheduling models that have a different, usually broader model scope. In this way, business aspects across multiple sites or across a business unit can be reflected at the unit optimization level.

The model scope greatly effects the requirements for process economics. The boundaries define the required input and modeling associated with pricing. By selecting different model scope or model method, the pricing can be made easier or near impossible. For example, streams and products that are bought or sold externally to the business unit are far easier to price than streams and products that are internal to the business unit or company. Also, it would result in less information to validate the model if one tries to price a stream without measurements. Since the optimization algorithm is making relative trade-offs to optimize the objective function, the pricing or costing should be on a marginal basis.

13. OFFLINE AND ONLINE USAGE

Models used in an offline environment have less stringent requirements since the user is responsible for the validity of the input and output, whereas in online environments models and their surrounding support software must handle validity automatically. Additionally, models used online typically must be more robust to solve across sometimes rather wide ranges of operating conditions. Commissioning an online model application can take as much as one-third more effort compared to developing a model for offline usage.

Today's online model applications can sense conditions that indicate what equipment is in operation or out of service, and how equipment is configured (''lined up''). ''Presolve'' logic, based on measured data, automatically turns equipment models on and off and configures equipment model interconnections and values correctly. Posing the

correct problem for the moment in an online system is an important part of its application's requirements.

14. MODEL MAINTENANCE

Maintenance of large size, high fidelity online applications needs to be considered in the same way maintenance of any other model-based operations improvement or process control application is handled. First of all, commissioning cannot be considered complete until the system is robust under normal operating conditions and during changes in operating conditions and/or plant configuration that will occur even if only relatively infrequently. It is necessary to run two cases every optimization cycle. The first case uses observed conditions to update equipment and process performance parameters to make the model solution best match actual operation. The second case uses the elucidated equipment performance factors along with all other model equations to better predict how dependent conditions will change with manipulation of independent DOFs. In the first Parameter or Reconcile case, observed conditions are used to *automatically* ''pose the right problem,'' a very important task that exists in online model applications but is not required when doing offline modeling. All equipment that can come on or off line, and all reconfiguration of piping lineup have to be anticipated so that proper action can be taken to use available data to pose the right problem. This set of tasks of posing the right problem is at times referred to as run time initialization or RTI. An integral part of the model, RTI logic is executed in scripts after online data is fetched and before the Parameter or Reconcile case is executed. Quite complex yet robust RTI logic is employed in online systems. For example, in an olefins plant there are typically 10 to even 20 steam crackers in the plant, some of which are typically out of service for decoking. Also, each steam cracker online may be lined up to use different feedstocks. RTI logic uses observed data to pose the right problem for all the possible combinations of these on/off situations and feedstock configurations. Far more project execution time is spent on handling abnormal operating conditions than for normal operating conditions. A Reconcile case can be posed to improve model robustness since imperfect data can be better processed while maintaining reasonable results. Reconciliation can help where decisions cannot be made from raw data alone, but only when this data is used to solve the model equations. For example, raw temperature and flow measurements may indicate that a heat exchanger has a ''temperature cross'' that violates the Second Law of Thermodynamics. The solution can be forced to honor Second Law

constraints by lower bounding temperature crosses to be slightly larger than zero, and measured flows and temperatures can be reconciled slightly from their observed values to allow these constraints to be honored. Weighting of measurement confidence limits during reconciliation should reflect normal instrument error. Once a model-based application is commissioned with robust performance, maintenance will be limited to infrequent changes in plant equipment, instrumentation, and piping lineup. Most maintenance can be expected to occur after a major plant turnaround. EO modeling, because of its simultaneous solution approach makes adding, deleting, or changing a part of a complex model easier than if SM methods were used, since SM methods require attention to the order in which they are solved, and employ many nested convergence loops that have to be modified when changes are made.

15. EXAMPLES OF INDUSTRIAL APPLICATIONS

Since the advent of efficient and robust simulation and optimization solution ''engines'' and flowsheeting software packages that allow for relatively easy configuration of complex models, numerous integrated, high fidelity, and multiscale process model applications have been deployed in industrial plants to monitor performance and to determine and capture improvements in operating profit.

Well over 50 large-scale EO model-based RTO applications have been deployed for petroleum refining processes. These model applications have been deployed in petroleum refineries Liporace *et al.*, 2009; Camolesi *et al.*, 2008; Mudt *et al.*, 1995, both on separation units (crude atmospheric and vacuum distillation units) and on reactor units (including fluidized catalytic crackers (FCC), gasoline reformers, and hydrocrackers).

Petrochemical plants, especially olefins plants that can manufacture numerous products in different proportions from the same feedstock, have had probably the greatest success at delivering value from sophisticated online plant-wide models Cutler and Perry, 1983; Rejowski *et al.*, 2009; Paules and Meixell, 1994; Fatora and Ayala, 1992; Fatora *et al.*, 1992a; Fatora *et al.*, 1992; Houk *et al.*, 1992; Kelly *et al.*, 1991. Over 50 ethylene RTO applications have been deployed, as well as several others on nonolefin petrochemical processes.

Chemical plants that have small conversion per pass, large expensive recycle ratios (typically vapor, requiring recompression), selectivities and yields that are not close to ideal, and which have parallel reactors, for instance, also have proven to be good candidates for plant-wide optimization applications. Well over 30 of these plant-wide applications

are in use today Mercangöz and Doyle, 2008; Lowery *et al.*, 1993; Meixell and Tsang, 1988. Microkinetics-based reactor models Dumesic *et al.*, 1993, have been deployed in several online, plant-wide optimization applications (e.g., in an ethylene oxide plant using a published reaction mechanism Stegelmann *et al.*, 2004) with good success. These reactor models span the scales from surface chemistry to macroscopic selectivity improvements, which result in significant reduction of feedstock usage. The microkinetics approach is basically addressing what has traditionally been done by mathematical manipulation of reaction mechanism relationships to arrive at closed form reaction rate expressions. By numerically dealing with more open forms of the same mechanisms, reaction models can be more easily developed with fewer assumptions, and can be more easily modified, maintained, and understood.

On the modeling level, there are several elements required to deliver success and sustain benefits. They include opportunity for improvement, DOFs (independent conditions) manipulated across an effective range, and trade-offs must exist for optimization modeling applications to deliver benefits. There are additional critical success factors, beyond the modeling level, for successful modeling applications in industry. Summarized in Table 1, these critical success factors include but are not limited to having a process control system to support online application, integration of business processes and operations, long-term focus

Table 1 Critical success factors for successful modeling applications

Model objectives	Sufficient functionality and resolution for present objectives are included. Path for expanding scope is thought about so ''dead ends'' are avoided
Modeling technology	Equation-oriented models and large scale solvers for speed, robustness, and maintainability
Model accuracy	Rigorous process operations and physical properties for accuracy
Model consistency	Integration with offline modeling
Model constraints	Correct limits and bounds
Control system	Effective multivariable process control system in place for online applications
Planning/ scheduling	Integration of business processes, operations, and pricing
Sustained performance	Long-term focus with clearly defined resources to sustain benefits
Skill set	Many disciplines are required
Metrics	Continual auditing process in place

for sustained performance, skill set of the organization, and continuing auditing process for performance metrics.

16. CO_2 CAPTURE WITH AQUEOUS ALKANOLAMINE SOLUTION

The model for CO_2 capture section of a chemical plant is used as an example to illustrate integrated, high fidelity, multiscale process models that are being applied to improve plant operations. CO_2 capture by absorption with aqueous alkanolamines represents an especially relevant modeling study these days because it is considered a key technology to reduce CO_2 emissions from fossil-fuel fired power plants and other CO_2 emitters to help alleviate global climate change Rochelle, 2009; Zhang *et al.*, 2009. The demonstrated success in deploying this CO_2 capture model online is an important milestone toward future use of similar models configured and used to help reduce CO_2 emissions in the most economical manner from power plants, chemical plants, and refinery CO_2 emission sources.

Figure 3 shows a comprehensive CO_2 capture process model, which involves thermophysical property and reaction kinetic models for CO_2

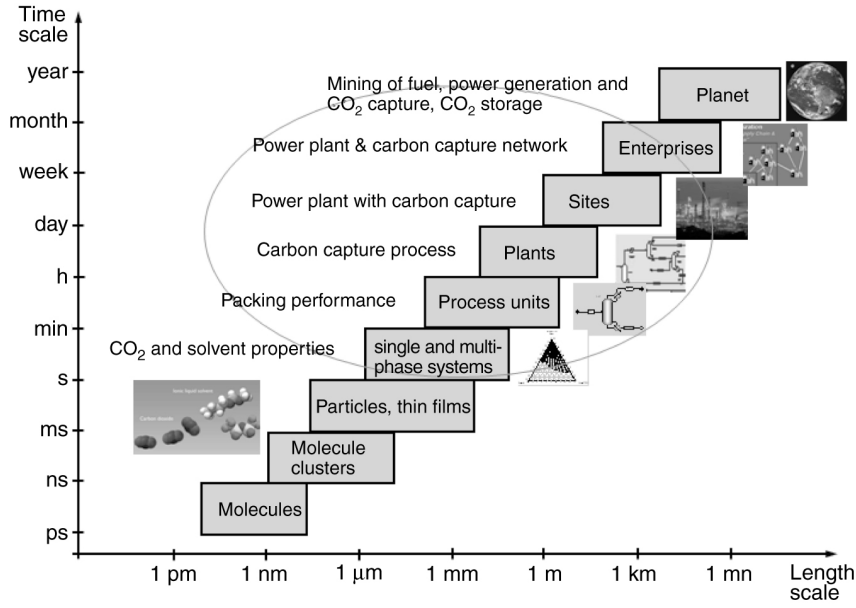

Figure 3 Integrated, high fidelity, multiscale process modeling of CO_2 capture and storage. Modified based on "Beyond the Molecular Frontier," NRC report (2003).

and absorption solvents, tray or packed column performance models for the absorber and the stripper, models for CO_2 absorption and solvent regeneration process, models for chemical or power plants integrated with the CO_2 capture process, and on a larger scale, network of chemical or power plants with CO_2 capture process, CO_2 transportation pipeline, and CO_2 storage reservoirs.

17. MODELING CO_2 AND ABSORBENT PHYSICAL PROPERTIES AND CHEMICAL REACTIONS

Numerous chemical solvents including carbonates, ammonia, and alkanolamines have been or are being developed for CO_2 capture. The CO_2 capture process examined in this study makes use of an aqueous solution of *n*-methyldiethanolamine (MDEA), activated with piperazine (PZ). Figure 4 shows the molecular structure of MDEA and PZ. MDEA is a tertiary amine. Upon absorbing CO_2, MDEA associates with hydronium ion H_3O^+ to form a protonated MDEA ion $MDEAH^+$. PZ is a cyclic amine. It can also associate with H_3O^+ to form a protonated ion PZH^+, and react with CO_2 to form a carbamate ion $PZCOO^-$ and a dicarbamate ion $PZ(COO)_2^{2-}$. In all, for the CO_2 capture system with MDEA/PZ, there are nine ionic reactions that take place in the aqueous solution. Table 2 shows the nine aqueous phase reactions. Resulting from the aqueous phase reactions are four cations (H_3O^+, $MDEAH^+$, PZH^+, $HPZH^{2+}$), five anions (OH^-, HCO_3^-, CO_3^{2-}, $PZCOO^-$, $PZ(COO)_2^{2-}$), and one zwitterion ($^+HPZCOO^-$).

Table 3 shows the 19 chemical species considered in the model, that is, 5 inert gases, CO_2 to be absorbed, solvent water, MDEA, and PZ amines, and 10 ionic species. All ionic species, zwitterion included, exist only in the liquid phase. The vapor phase components are mainly inert, that is, supercritical components that dissolve sparingly into the liquid.

Among the nine chemical reactions that occur in the aqueous solution, chemical equilibrium is only attained for six of the reactions. The

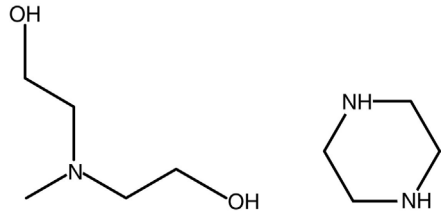

Figure 4 Molecular structure of *n*-methyldiethanolamine (MDEA) and piperazine (PZ).

Table 2 Aqueous phase reactions for CO_2 capture with aqueous MDEA/PZ solution

Reaction	Equilibrium controlled or kinetics controlled	Stoichiometry
1	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
2	Equilibrium	$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$
3	Equilibrium	$MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$
4	Equilibrium	$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
5	Equilibrium	$HPZH^{2+} + H_2O \leftrightarrow PZH^+ + H_3O^+$
6	Equilibrium	$^+HPZCOO^- + H_2O \leftrightarrow PZCOO^- + H_3O^+$
7	Kinetic	$CO_2 + OH^- \leftrightarrow HCO_3^-$
8	Kinetic	$PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
9	Kinetic	$PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO)_2^{2-} + H_3O^+$

Table 3 Chemical species considered for CO_2 capture with aqueous MDEA/PZ solution

Abbreviation	Name	Chemical formula
H_2	Hydrogen	H_2
N_2	Nitrogen	N_2
Argon	Argon	Ar
CH_4	Methane	CH_4
CO	Carbon monoxide	CO
CO_2	Carbon dioxide	CO_2
H_2O	Water	H_2O
MDEA	Methyldiethanolamine	$C_5H_{13}NO_2$
MDEA+	$MDEA^+$	$C_5H_{14}NO_2^+$
HCO_3^-	HCO_3^-	HCO_3^-
CO_3^{2-}	CO_3^{2-}	CO_3^{2-}
H_3O^+	H_3O^+	H_3O^+
OH^-	OH^-	OH^-
PZ	Piperazine	$C_4H_{10}N_2$
PZH^+	PZH^+	$C_4H_{11}N_2^+$
$HPZH^{2+}$	$HPZH^{2+}$	$C_4H_{12}N_2^{2+}$
HPZCOO	HPZCOO	$C_5H_{10}N_2O_2$
$PZCOO^-$	$PZCOO^-$	$C_5H_9N_2O_2^-$
$PZ(COO)_2^{2-}$	$PZ(COO)_2^{2-}$	$C_6H_8N_2O_4^{2-}$

three capture reactions of CO_2 with OH^-, PZ, and $PZCOO^-$ are kinetics controlled.

Accurate thermodynamic modeling is essential for meaningful process modeling and simulation of the CO_2 capture system with aqueous amine solutions Zhang and Chen, 2011. To accurately describe thermophysical properties of the CO_2-loaded aqueous amine solutions, one must explicitly account for the solution chemistry, that is, the chemical equilibria of the nine ionic reactions summarized in Table 2. In addition, activity coefficients play a key role in phase equilibrium calculations, liquid phase chemical equilibrium calculations, and in calculations for heat of CO_2 absorption, liquid heat capacity, liquid enthalpy, pH, and so on. Rigorous electrolyte thermodynamic models need to be applied as the electrolyte solutions are known for the highly nonideal liquid phase behavior resulting from the long-range ion–ion interactions and the short-range molecule–molecule, molecule–ion, and ion–ion interactions in the liquid phase. The most common choice is the electrolyte NRTL (nonrandom two-liquid) activity coefficient model Song and Chen, 2009.

Figure 5 shows comparison of the predicted CO_2 partial pressures for the MDEA–CO_2–water system with the experimental data of Jou

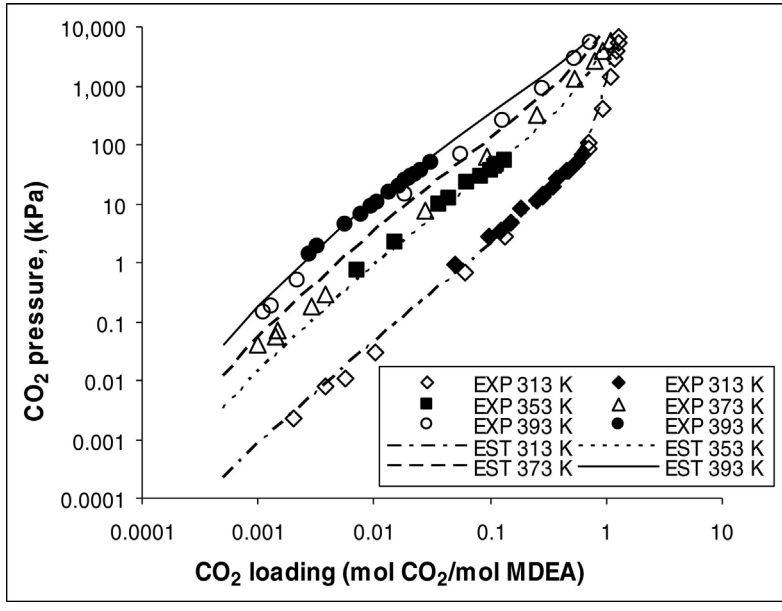

Figure 5 Vapor–liquid equilibrium of MDEA–CO_2–H_2O (MDEA mass fraction at

et al. (1982) and Ermatchkov *et al.* (2006). The model predictions on CO_2 partial pressure, species concentrations, heat of absorption, heat capacity, and enthalpy must be validated for the aqueous amine solutions before the activity coefficient model can be used for process modeling and simulation.

Apparent rate expressions are available to describe the reaction kinetics for the forward and reverse reactions of the three CO_2 capture reactions, that is, reactions 7–9 shown in Table 2, Bishnoi and Rochelle, 2002, Further mechanistic enhancements to the rate expressions are forthcoming through use of zwitterions (i.e., $^{+}HPZCOO^{-}$), first proposed by Caplow (1968) and later reintroduced by Danckwerts (1979).

18. MODELING CO_2 CAPTURE PROCESS

Figure 6 shows a simplified CO_2 capture process with two major process units: absorber and stripper Zhang *et al.*, 2009. A lean amine solvent (low CO_2 loading) is fed into the top of the absorber and is in countercurrent contact with the gas containing CO_2. The CO_2 is chemically absorbed by the amine solvent and the treated gas exits the top of the absorber. The rich (high CO_2 loading) amine leaves the bottom of the absorber and is preheated by a cross heat exchanger before

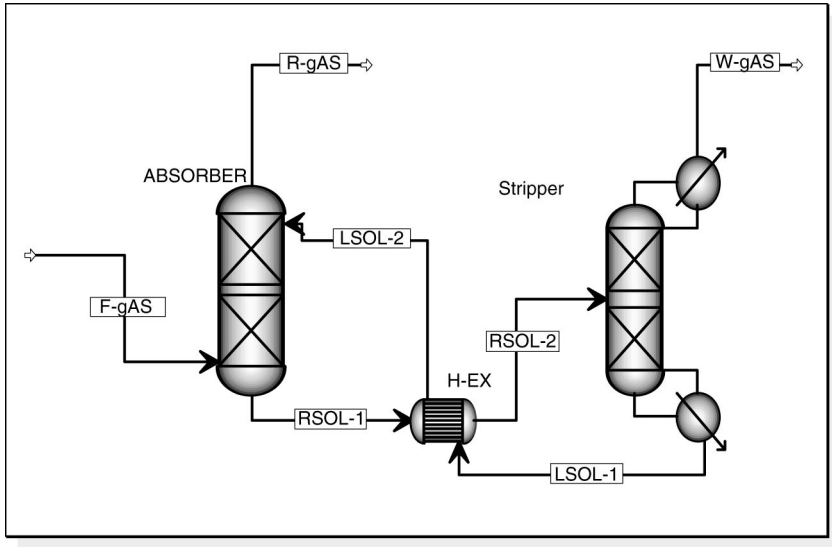

Figure 6 Typical CO_2 capture unit with absorber and stripper.

entering the top of the stripper. At stripper conditions, typically at higher temperature, the reaction between the amine and CO_2 is reversed, liberating the CO_2. A concentrated CO_2 stream is obtained from the top of the stripper. The lean solvent from the stripper is cooled and goes back to the absorber.

There are two well-established approaches in modeling performance of tray or packed columns used for the absorber and the stripper. They can be modeled either with the simpler traditional equilibrium-stage approach or more rigorous and higher fidelity rate-based modeling approach Zhang *et al*., 2009. The traditional equilibrium-stage models assume each theoretical stage is composed of well-mixed vapor phase and liquid phases and these two bulk phases are in phase equilibrium with each other. Tray ''efficiencies'' can be introduced to improve matching with column performance data. Although considered at times to be an adequate approximation for heat and mass balance calculations, this equilibrium-stage assumption yields inadequate model fidelity in modeling performance of chemical absorption columns where the contacting phases are far from in equilibrium. In contrast, rate-based multistage separation models assume that separation is caused by heat and mass transfer between the contacting phases; phase equilibrium is achieved only at the vapor–liquid interface, and the Maxwell–Stefan theory is used to calculate mass transfer rates.

In rate-based multistage separation models, separate balance equations are written for each distinct phase, and mass and heat transfer resistances are considered according to the two-film theory with explicit calculation of interfacial fluxes and film discretization for nonhomogeneous film layer. The film model equations are combined with relevant diffusion and reaction kinetics and account for the specific features of electrolyte solution chemistry, electrolyte thermodynamics, and electroneutrality in the liquid phase.

Specifically the mathematical model for rate-based multistage separation model consists of the following equations for each stage: (1) material balances for bulk liquid, bulk vapor, liquid film, and vapor film, (2) energy balances for bulk liquid, bulk vapor, liquid film, and vapor film, (3) phase equilibrium at the interface, (4) summations, (5) mass fluxes for liquid film and vapor film, and (6) heat fluxes for liquid film and vapor film. Reaction terms are accounted for in the material balance equations. The Maxwell–Stefan multicomponent mass transfer equations are used to describe the mass fluxes. A driving force due to electric potential in each liquid film region is introduced to satisfy electroneutrality conditions at the boundary of the film region. When the films are discretized to account for enhanced transfer rates due to reactions, equations of material balances, energy balances, mass

fluxes, and heat fluxes are formulated and solved for each discretized film segment.

Figure 7 illustrates the discretized liquid film for CO_2 transfer across the vapor and liquid films. Here Y is gas phase composition, X is liquid phase composition, T is temperature, I is interface, V is vapor, and L is liquid. Note that the liquid film is discretized into multiple film segments to accurately model the nonhomogeneous film layer.

Figure 7 further shows that, as gaseous CO_2 moves up the absorber, phase equilibrium is achieved at the vapor–liquid interface. CO_2 then diffuses through the liquid film while reacting with the amines before it reaches the bulk liquid. Each reaction is constrained by chemical equilibrium but does not necessarily reach chemical equilibrium, depending primarily on the residence time (or liquid film thickness and liquid holdup for the bulk liquid) and temperature. Certainly kinetic rate expressions and the kinetic parameters need to be established for the kinetics-controlled reactions. While concentration-based kinetic rate expressions are often reported in the literature, activity-based kinetic rate expressions should be used in order to guarantee model consistency with the chemical equilibrium model for the aqueous phase solution chemistry.

Success of rate-based multistage separation modeling is ultimately tied to underlying equipment hydrodynamics performance correlations for tray or packed columns. For example, the thickness of the film

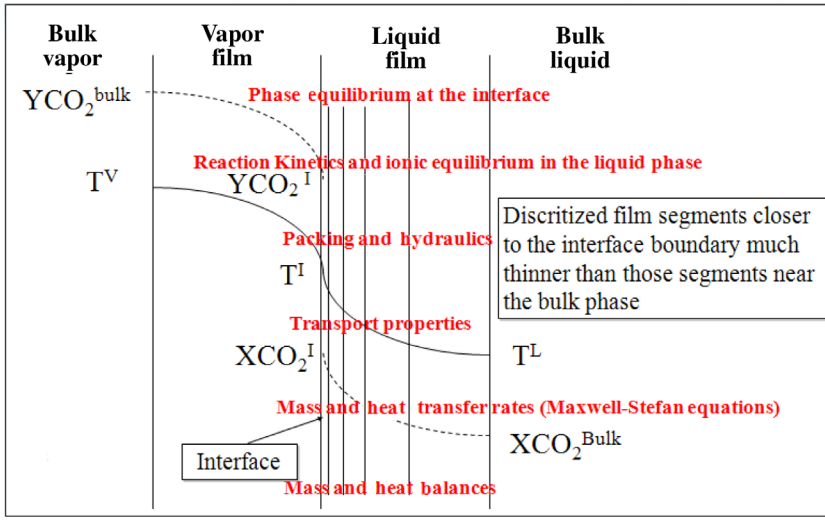

Figure 7 Discretized liquid film for CO_2 capture with chemical absorbent.

in each phase is computed as the ratio of the average diffusivity and the average mass transfer coefficient. In the case of packed columns operated countercurrent-wise, correlations are required for the mass transfer coefficients, the effective mass transfer area, the pressure drop, and the flood capacity of the column. Dependable and dimensionally consistent equipment performance correlations validated for modeling of CO_2 capture with aqueous amines have recently been developed for random and structured packing families Hanley and Chen, 2011. Used in rate-based calculations for columns, these performance correlations form part of the underlying equations for accurate modeling of the absorber and the stripper. They require information on packing or tray types and geometries along with transport properties such as surface tension, viscosity, density, diffusivity, and thermal conductivities.

19. MODELING CO_2 CAPTURE PROCESS AND THE PLANT

The example CO_2 capture process, shown in Figure 8 as an Aspen Plus EO model representation, is part of an ammonia plant. Designed to scrub CO_2 from ammonia synthesis gas, it includes an absorber and two solution regeneration columns, one stripping the rich, CO_2 laden solution leaving the absorber to semilean concentration of absorbed CO_2, and the other cleaning the solution even further to lean solution

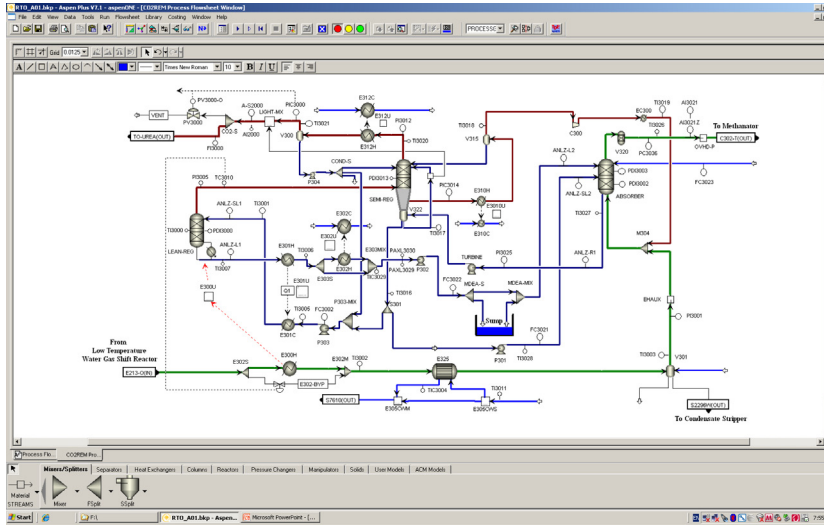

Figure 8 Aspen Plus EO model for an MDEA/PZ CO_2 capture unit.

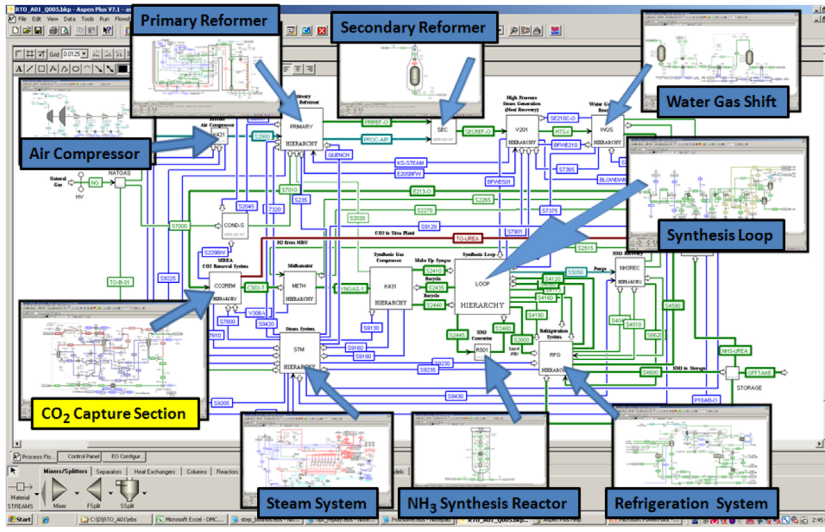

Figure 9 Aspen Plus EO model for an ammonia plant.

quality. In addition, there are the associated heat exchangers, pumps, a power recovering expander, and flash drums. Figure 9 shows the hierarchy-level model representation for the Aspen Plus EO ammonia plant model. The CO_2 capture unit model is shown only as a hierarchy block in the ammonia plant model. Other blocks in the plant model represent other major process units such as air compressors, primary reformer, secondary reformer, water gas shift, methanator, ammonia synthesis loop, refrigeration loop, and steam system.

The gas being scrubbed of CO_2 is ammonia synthesis gas, a mixture of hydrogen and nitrogen in about a 3:1 ratio with small amounts of methane, CO, and argon present. The gas entering the absorber has about 18 mol% CO_2 and the gas leaving the absorber ranges in CO_2 content from about 2 to 500 ppm by volume, depending on plant rate and the performance of the solution regeneration equipment, which is affected significantly by numerous factors, including among others, cooling water temperature, solution strength, and heat exchanger fouling.

The gas composition is optimized with DOFs outside the CO_2 scrubbing system with regard to inert composition (methane and argon) and hydrogen to nitrogen ratio since the levels of these components affect downstream (ammonia synthesis) reaction kinetics. Improved kinetics at lower inert levels are achieved at the expense of using more fuel or feedstock, since lower inerts can be achieved by firing the primary

reformer harder upstream of the CO_2 system, or more purge can be used downstream from the synthesis loop to lower the inerts level. Similarly, the optimum nonstoichiometric H_2:N_2 ratio in the gas is determined using high fidelity reaction kinetics that account for the rate-limiting step being the adsorption of nitrogen onto the heterogeneous promoted magnetite catalyst. Constraints may limit the range of operating conditions allowable, and active constraints profoundly affect the optimization results. This situation gives rise to classical optimization trade-offs that are only quantifiable with a high fidelity plant-wide model.

The separation models for absorber and regenerators were first developed as equilibrium models without the activating PZ component, and then were enhanced to include PZ and were migrated to rate-based (kinetic and mass transfer rate limited) models. Many of the modeling configuration and robustness issues were addressed in the simpler models. These issues included several material balance as well as numerical stiffness challenges that are not intuitively obvious. Most of the issues related to model specification and use of industrial data were solved with the equilibrium-based models. The model of the illustrated flowsheet, along with the complete upstream and downstream equipment models for the entire ammonia plant, was deployed online before upgrading the separation models. Data consistency and several very important modeling details would have been more difficult to identify and fix had the more complex rate-based model been deployed first.

EO models require that the problem be well specified since the whole system is solved simultaneously. SM techniques are more forgiving and allow less well posed problems to be solved since inconsistencies may only become apparent when the whole system is solved together. It became apparent that a makeup stream was necessary for MDEA since although only tiny amounts of MDEA leave with the scrubbed synthesis gas and with the recovered CO_2, the simultaneous solution could not close the material balances to normally used very close tolerances without the makeup stream. The makeup stream has to be dependent since the solution must seek out the makeup amount to just offset the miniscule MDEA losses dictated by vapor–liquid equilibrium and approach to equilibrium. There must be a dependent water makeup stream for the same reasons. Also, even with these additions the almost total recycle nature of the circulating solution causes the simultaneous solution to be difficult to solve robustly at different operating conditions. A very small purge of the solution, as is done in the plant by filters removing degradation products, makes the model very robust. The model has been running for several months in open loop, cycling from parameter estimation to optimize case modes with very

few failures. Closed loop commissioning will occur in a few months. CO_2 slip from the absorber can be changed by several hundred parts per million from Parameter case to Parameter case, and the plant rate may change quite significantly (15–20%) and the model solves without problems. Prior to addressing data consistency, model specification, and configuration (makeup MDEA, makeup water) issues the model was not fit for in-the-plant use. These issues were repaired offline before any attempt was made to deploy the model in the plant environment. Significant economic benefits have been identified and will be thoroughly investigated prior to closed loop operation.

Execution times for the overall ammonia plant model, of which the CO_2 capture system is a small part, are on the order of 30 s for the parameter estimation case, and less than a minute for an Optimize case. The model consists of over 65,000 variables, 60,000 equations, and over 300,000 nonzero Jacobian elements (partial derivates of the equation residuals with respect to variables). This problem size is moderate for RTO applications since problems over four times as large have been deployed on many occasions. Residuals are solved to quite tight tolerances, with the tolerance for the worst scaled residual set at approximately 1.0×10^{-9} or less. A scaled residual is the residual equation imbalance times its Lagrange multiplier, a measure of its importance. Tight tolerances are required to assure that all equations (residuals) are solved well, even when they involve, for instance, very small but important numbers such as electrolyte molar balances.

The overall cycle time from sensing that the plant is reasonably close to steady-state conditions, fetching and validating data, posing the appropriately configured problem (using initialization logic based on observed data), solving the parameter estimation case, and then the Optimize case takes less than 5 min. This overall plant model includes rigorous reaction rate-based models for all the major reactors, including the primary and secondary steam reformers, high- and low-temperature water gas shift reactors, a methanator, and a multibed ammonia synthesis reactor. The process, refrigeration, steam, and fuel/flue gas parts of the plant are all included in the plant-wide model. All compressors and their steam turbine drivers are modeled with predictive relationships. All the recycle streams are closed and solved very efficiently using the EO simultaneous solution approach.

For the CO_2 capture system, the parameter cases update all significant equipment performance to match observed data. The primary performance of this system is the CO_2 absorber slip and the energy required to regenerate the solution to semilean and lean solution quality. The model can be made to match observed performance in several ways. Measurements are available for the lean and semilean

solution CO_2 content (with all CO_2-bound species expressed as mass percent CO_2). The semilean and lean solution columns are forced to deliver solution with the observed quality by adjusting liquid holdup (affecting residence times and therefore reaction effects) and interfacial areas (affecting mass transfer rates). Holdup and interfacial areas are determined from correlations for specific packing families or trays (depending on the equipment configuration) but these correlations are not precise predictors. Adjustment can be made to only one parameter in any one of these correlations (usually a multiplier factor), or reconciliation can be employed to distribute the model–data mismatch among more than one correlation. Sensitivity analysis is useful for determining reasonable ranges for the parameters (factors). For packing the height equivalent to a theoretical plate (HETP) needs to be reasonable to have meaningful adjustments to correlations to match observed performance. Even lean and semilean flow rates may have associated errors and offsets or multipliers to these flows can be simple parameters used to match the model results to observed data. The best way to determine the best choice of parameters to update every Parameter case cycle is to analyze multiple data sets simultaneously as part of the commissioning effort. These data sets should be at different operating conditions. A set of parameters with the least deviation from ''ideal'' (typically a factor of 1.0) that can best match several data sets at different conditions is desirable.

Optimization cases are done only with the overall plant model (with any unit operations that are out of service turned off in the model automatically using logic based on measured data). The CO_2 absorber cannot leak out too much CO_2 since the absorber overhead stream goes to a methanator that will overheat with too much CO_2 in its feed. This situation can occur rapidly and can cause the plant to have to vent synthesis gas before the methanator—a costly incident. The overall plant optimization case objective function is operating profit, so the DOF in the CO_2 scrubbing area and those upstream that affect the operating profit include those that must keep the CO_2 slip to an acceptable level using the least costly utilities, while delivering the most CO_2 to the urea plant. Far upstream in the process, the primary reformer feed steam to carbon (S/C) ratio is many times most economical to minimize (the primary reformer fuel usage is reduced), but the excess steam in the process provides the lean solution regenerator heat, so the S/C ratio cannot be reduced below that needed to sufficiently regenerate the solution to allow adequate absorber performance. A high fidelity model operating online in conjunction with a multivariable, predictive, advanced control system makes these trade-offs often and allows the plant to continuously operate closer to the optimum.

The Optimize case executes about 12 times per day, sufficient to capture differences in the optimum set of operating conditions due to ambient and cooling water temperatures, changing natural gas composition, and operational mode changes imposed by external business decisions and feed gas availability. The maximum number of executions per day is not set by computing times, but is set by the aforementioned conditions as well as the settling time of the ammonia plant. The advanced control system accepts new external targets after each optimization cycle, moves the plant to these conditions, and holds these conditions until new targets are received. Most external targets are intensive conditions such as feed steam to carbon ratio, temperatures, and compositions or composition ratios (i.e., synthesis gas H_2 to N_2 ratio). Extensive conditions such as flow rates can be continuously manipulated by the control system to allow, for instance, maximum production to be sought out, if desired, between optimization executions.

Ammonia plants are linked to the ambient conditions more closely than many plants since the process air compressor (supplying the nitrogen for the synthesis gas and the oxygen for the autothermal secondary reformer) is significantly affected by ambient temperature. Another trade-off that the optimizer exploits is the best distribution of the very high pressure (120 kg/(cm^2 g)) steam between the ammonia plant synthesis gas steam turbine driver and a similar driver of the urea plant CO_2 compressor. There is very close coupling among the S/C ratio, very high-pressure steam generation using waste heat recovery, the CO_2 removal system performance, and other key operating conditions.

20. MODELING SITE-WIDE CHEMICAL COMPLEX

Shown in Figure 10, this ammonia plant is a major part of the overall fertilizer site complex. Other major facilities include urea plant, steam system, and cooling water system. Most of the ammonia is used to make granulated urea product. The other raw material for urea synthesis is CO_2 from the CO_2 capture system in the ammonia plant, supplemented with a small stream from an adjacent business. The ammonia production and the CO_2 available from the ammonia plant are never precisely in balance, in part because of the overall stoichiometric yields of ammonia and CO_2 from the natural gas feedstock. CO_2 is the limiting feedstock for the urea plant and its production rate in the ammonia plant sets the urea plant production rate since there is no intermediate CO_2 storage to buffer the urea production from the CO_2 production rate. Ammonia that is produced in excess of that which is used to make urea

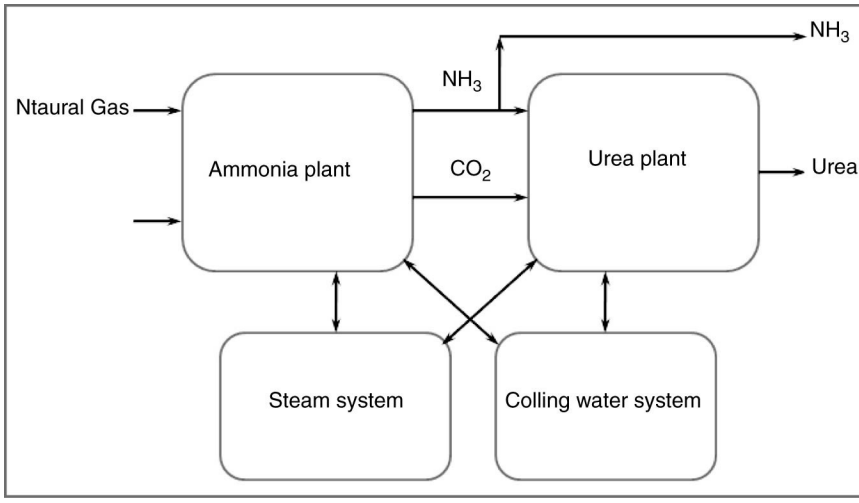

Figure 10 A fertilizer site complex.

is sent to refrigerated storage, and sold. The ammonia and urea plants are not only integrated with raw material streams but are strongly coupled by the site steam system, and less critically, through the cooling water system. Both the synthesis gas compressor in the ammonia plant and the CO_2 compressor in the urea plant use the highest pressure steam available at the site, 112 bar steam, generated from waste heat recovery in the ammonia plant. These two turbines are the only consumers of this ''very high-pressure'' steam. As the plants' production rates increase the total power demand in these turbines increases faster than the 112 bar steam production. When the 112 bar letdown valve to the 48 bar steam header approaches being closed, both the ammonia and urea plants cannot increase their production rates since the utility boiler supplies 48 bar steam—112 bar steam is only generated by waste heat recovery. The urea plant production can be increased by venting ammonia plant synthesis gas before the compressor (thus not increasing its power demand), and increasing the front-end rate of the ammonia plant to produce more CO_2. This operating mode is costly, but the overall plant economics are more favorable at these higher urea production rates than at lower rates. The optimization model includes a simplified but rigorously correct urea reactor to account for stoichiometric consumption of both ammonia and CO_2. Additionally, the model includes a detailed rigorous model of the CO_2 compressor and its steam turbine to allow trade-offs among the power demands of this turbine, the ammonia synthesis gas turbine, and the steam generation

from waste heat recovery. Significant savings have been identified through the strategy of increasing the steam-to-carbon ratio in the ammonia plant, which requires more fuel usage in the primary reformer, but generates significantly more 112 bar steam by recovering a large portion of this energy. This allows higher ammonia and urea plants rates to be achieved without venting synthesis gas. The optimization model includes a quite detailed model of the site steam system, not only at the highest steam pressure levels but also of all the steam headers, all the way down to the condensate recovery levels. The 48 bar steam utility boiler is modeled, including its fuel and combustion air system. The strategy employed when defining the model scope was to include sufficient site-wide facilities to honor important constraints, to exploit available trade-offs, and to account for the effects of the optimization system directly, and not solely through feedback.

This application illustrates that integrated, high fidelity, multiscale models from molecular level to site-wide complex can be deployed in nonideal online environments to deliver benefits and insight that cannot be elucidated with simpler, less rigorous, more empirical models.

21. SUMMARY

Efficient and robust process models of chemical plants and refineries deliver benefits by making accurate trade-offs often that cannot be determined through other means. These models must be quite accurate in areas that affect economics and feasibility to determine benefits that can be captured, that while large, are small percentages of the overall operating profit. Rigorous, mechanistic models satisfy the required accuracy, but even these are greatly improved by using measured plant data to update model parameters. Models of appropriate heterogeneous fidelity and scale must be integrated to keep model development costs down while still being able to identify actionable profitable changes in conditions. EO simultaneous solution techniques make it possible to solve highly complex models in industrial environments efficiently and very robustly. The nature of the optimal solutions is that they will be at many simultaneous constraints, so an advanced process control application (typically model based, predictive, and multivariable) is needed to impose the determined solution onto the operating plant.

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